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SYNTHESES INVOLVING ORGANOMETALLIC AND ORGANOMETALLOIDAL COMPOUNDS CONTAINING POLYFLUORO AND POLYCHLORO SUBSTITUENTS

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SYNTHESES INVOLVING ORGANOMETALLIC
AND ORGANOMETALLOIDAL COMPOUNDS CONTAINING
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FOREWORD

This report was prepared by Iowa State University of Science and Technology, Ames, Iowa, under USAF Contract No. F33615-69-C-1046. This contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena", Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials". The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Christ Tamborski (AFML/LNP) Project Scientist.

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This technical report has been reviewed and is approved.



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ABSTRACT

The primary objective is concerned with new or improved syntheses of organometallic and organometalloidal compounds containing polyfluoro and polychloro substituents. These versatile reagents are to be used for the preparation of thermally stable fluids, lubricants, etc. One of the goals is to make available organometallic compounds of general types such as $\text{CF}_3(\text{CF}_2)_n\text{-M}$ and $\text{M-(CF}_2)_n\text{-M}$, in which M represents a metal or a metalloid. In addition, perhaloorganometallic compounds containing heteronuclear systems such as pyridine and thiophene have been studied. These two studies admirably complement each other, for there has been developed from the perhalogenated thiophenes some novel and highly promising routes to the perhalogenated alkanes.

TABLE OF CONTENTS

	Page
SECTION I	
GENERAL INTRODUCTION	1
SECTION II	
REACTIONS OF SOME POLYHALOPYRIDINES WITH ORGANOMETALLIC COMPOUNDS	3
1. INTRODUCTION	3
2. RESULTS AND DISCUSSION	4
3. EXPERIMENTAL	6
a. Reaction of 2,5-dichloropyridine with <u>n</u> -butyllithium and subsequent reaction with derivatizing reagents	6
(1) Reaction of 2,5-dichloropyridyl-lithium with solid carbon dioxide	6
(2) Reaction of 2,5-dichloropyridyl-lithium with chlorosilanes	6
(3) Reaction of 2,5-dichloropyridyl-lithium with carbonyl compounds	7
(4) Reaction of 2,5-dichloropyridyl-lithium with copper(I) halides in appropriate solvents, and subsequent treatment with acid chlorides	7
b. Preparation of 2,5,2',5'-tetrachloro-4,4'-bipyridyl	7
c. Reaction of 2,5-dichloropyridine with phenylmagnesium bromide	8
d. Reaction of 3,5-dichloropyridine with <u>n</u> -butyllithium and subsequent reaction with chlorotrimethylsilane	8
e. Metalation of 2,6-difluoropyridine with <u>n</u> -butyllithium	8
(1) In THF: 1:1 ratio of <u>n</u> -BuLi + 2,6-C ₅ F ₂ H ₃ N	8
(2) In THF: 2:1 ratio of <u>n</u> -BuLi to 2,6-C ₅ F ₂ H ₃ N	9
(3) In Ether: 1:1 ratio of <u>n</u> -BuLi to 2,6-C ₅ F ₂ H ₃ N	9

TABLE OF CONTENTS

	Page
SECTION III TRICHLORO-2-THIENYLMAGNESIUM HALIDE	17
1. INTRODUCTION AND DISCUSSION	17
2. EXPERIMENTAL	20
a. Preparation of trichloro-2-thienyl- magnesium halide	20
(1) From tetrachlorothiophene and magnesium by the entrainment technique (A recommended general procedure)	20
(2) From tetrachlorothiophene and copper-magnesium alloy	21
(3) From tetrachlorothiophene and magnesium in the presence of various catalysts	21
b. Attempted preparation of a di- Grignard reagent from tetrachloro- thiophene	21
(1) By the entrainment technique	21
(2) Use of copper-magnesium alloy	22
c. Stability of trichloro-2-thienyl- magnesium halide in THF	22
d. Reactions of trichloro-2-thienyl- magnesium halide with metal halides and miscellaneous reagents	22
e. <u>In situ</u> preparation of various 2-silyltrichlorothiophenes	22
SECTION IV TRICHLORO-2-THIENYLLITHIUM	28
1. INTRODUCTION AND DISCUSSION	28
2. EXPERIMENTAL	28
a. Preparation of trichloro-2-thienyl- lithium (I)	28
(1) Method A	29
(2) Method B	29
b. Carbonation	29
c. Reaction with chlorotrimethylsilane	30

TABLE OF CONTENTS

	Page
d. Reaction with chlorophenyldimethylsilane	30
e. Reaction with chlorotriphenylsilane	30
f. Reaction with dichlorodimethylsilane	31
g. Reaction with chlorodimethylhydrosilane	31
h. Reaction with chlorodiphenylphosphine	31
SECTION V 3,4-DICHLORO-2,5-DILITHIOTHIOPHENE	32
1. INTRODUCTION AND DISCUSSION	32
2. EXPERIMENTAL	32
a. Preparation of 2,5-dilithiodichlorothiophene	32
(1) Dichlorothiophene-2,5-dicarboxylic acid	33
(2) 2,5- <u>bis</u> (Trimethylsilyl)dichlorothiophene	33
(3) 2,5- <u>bis</u> (Dimethylhydrosilyl)dichlorothiophene	33
(4) Reaction of 2,5-dilithiodichlorothiophene and dimethyldichlorosilane	33
(5) Reaction of 2,5-dilithiodichlorothiophene and diphenylhydrochlorosilane	34
(6) Reaction of 2,5-dilithiodichlorothiophene and tetrachlorothiophene	34
SECTION VI TRICHLORO-2-THIENYLCOPPER	
1. INTRODUCTION AND DISCUSSION	37
2. EXPERIMENTAL	38
a. Preparation of trichloro-2-thienyl copper(I)	38
(1) Method I: In THF	38
(2) Method II: In ether/THF (1/1)	38
(3) Method III: In monoglyme	39
(4) Method IV: In ether	39

TABLE OF CONTENTS

	Page
(5) Method V: From lithium dimethylcuprate	39
(6) Method VI: By an <u>in situ</u> - entrainment method	39
SECTION VII 3,4-DICHLORO-2,5-DICOPPERTHIOPHENE	43
1. INTRODUCTION AND DISCUSSION	43
2. EXPERIMENTAL	43
a. Preparation of 2,5- <u>bis</u> (copper(I))di- chlorothiophene	43
(1) Preparation of 2,5- <u>bis</u> (acetyl)di- chlorothiophene	43
(2) 2,5-Diiododichlorothiophene	44
SECTION VIII CONVERSION OF C-SiMe ₂ H TO C-Li	45
1. INTRODUCTION AND DISCUSSION	45
2. EXPERIMENTAL	46
a. General Procedure	46
SECTION IX COUPLING REACTION OF SOME POLYHALOARYL- METALLIC COMPOUNDS WITH PHOSPHORYL CHLORIDE	50
1. INTRODUCTION AND DISCUSSION	50
2. EXPERIMENTAL	51
a. Preparation of copper compounds	51
b. Reaction of perhaloaryl copper compounds with POCl ₃	51
SECTION X PREPARATION OF PERHALOARYL IODIDES VIA PERHALOORGANOMETALLIC COMPOUNDS AND IODINE	54
1. INTRODUCTION AND DISCUSSION	54
2. EXPERIMENTAL	55
a. Preparation of polyhaloarylm metallic compounds	55
b. Preparation of alkylcopper compounds	56
c. Preparation of phenylcopper	56
d. Preparation of 'ate' complexes	56
e. Iodination of copper compounds	56

TABLE OF CONTENTS

	Page
(1) Iodination of aryl- and polyhaloaryl- copper compounds	56
(2) Iodination of alkylcopper compounds	57
(3) Iodination of 'ate' complexes	57
f. Iodination of perhaloarylmagnesium halides	57
g. Reactions of perhaloarenes with anhydrous sodium iodide	58
SECTION XI UNSYMMETRICAL PERHALOANALOGS OF BIPHENYL	66
1. INTRODUCTION AND DISCUSSION	66
2. EXPERIMENTAL	66
a. Preparation of polyhaloarylcopper compounds	66
b. Preparation of perhaloaryl iodides	66
c. Preparation of unsymmetrical perhalo-biaryls	66
SECTION XII CHLORINE-LITHIUM EXCHANGE UNDER VERY MILD CONDITIONS	72
1. INTRODUCTION AND DISCUSSION	72
2. EXPERIMENTAL	72

LIST OF TABLES

		Page
Table I	Reactions of 2,5-Dichloro-4-pyridyllithium with Some Derivatizing Reagents at -70°C	10
Table II	Reactions of 2,5-Dichloro-4-pyridylcopper ₂ with Some Acid Chlorides at -70°C	11
Table III	Spectroscopic Data of Various Compounds	12
Table IV	Analyses of Various Compounds	16
Table V	The Effect of Solvent and the Amount of Entrainer on the Yield of the Trichloro-2-thienylmagnesium halide	23
Table VI	Trichloro-2-thienylmagnesium Chloride from Tetrachlorothiophene and Various Copper-magnesium alloys	24
Table VII	Trichloro-2-thienylmagnesium Halide from Tetrachlorothiophene and Magnesium in the Presence of Various Catalysts	25
Table VIII	Reactions of Trichloro-2-thienylmagnesium Halide with Metal Halides and Miscellaneous Reagents	26
Table IX	<u>In situ</u> Preparation of Various 2-Silyltrichlorothiophenes	27
Table X	Spectral Data for Some Derivatives of 2,5-Dilithiodichlorothiophene	35
Table XI	Yields of 2-Acetyltrichlorothiophene by Various Methods	41
Table XII	Derivatives from Trichloro-2-thienylcopper	42

Table XIII	Reaction of Aryl and Polyhaloaryl Dimethyl- and Trimethylsilanes with Alkylmetallic Reagents in Ether	47
Table XIV	Reaction of Various Copper Compounds with POCl_3	52
Table XV	The Yields (%) of Different Iodides by the Reaction: $\text{RM} + \text{I}_2 \rightarrow \text{RI}$	59
Table XVI	The Yields (%) of RI and $\text{R}_2\overset{\text{a}}{\text{via}}$ (3) compared with the yields <u>via</u> (4) $\text{MR}_2\text{Cu}^{\text{b}} + \text{I}_2^{\text{c}} \rightarrow \text{RI} + \text{R-R} \quad (3)$ $\text{RCu}^{\text{b}} + \text{I}_2^{\text{c}} \rightarrow \text{RI} + \text{R-R} \quad (4)$	60
Table XVII	Effects of Temperatures, Solvent and the Type of Copper(I) Halide on the Yields (%) ^a of Iodobenzene and Biphenyl <u>via</u> $\text{PhLi}^{\text{b}} + \text{CuX} \xrightarrow{\text{TOC}} \text{PhCu} \xrightarrow[-78^\circ\text{C}]{\text{I}_2^{\text{c}}} \text{PhI} + \text{Ph-Ph}$	61
Table XVIII	Effects of Various Copper(I) Halides and Various Organometallics used to Prepare RCu on the Yields of RI (eqn. 5) $\text{RM} + \text{CuX} \rightarrow \text{RCu} \xrightarrow{\text{I}_2} \text{RI} + \text{R-R} \quad (5)$	62
Table XIX	Effects of Solvent for Iodine and also the amount of Iodine on the Yields of RI <u>via</u> $\text{RCu} \xrightarrow{\text{I}_2} \text{RI} + \text{R-R}^{\text{a}}$	63
Table XX	Variation in the Yields of RI with the Change of Temperature of Iodination ^a	64
Table XXI	Reaction of Perchloroarenes with Anhydrous Sodium Iodide	65
Table XXII	Some Unsymmetrical Perhalobiaryls <u>via</u> Perhaloarylcopper Compounds and Perhaloaryl Iodides	68

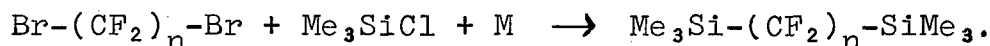
Table XXIII	Comparisons of the m.p. of Some Perhalogenated Symmetrical and Unsymmetrical Biaryls	69
Table XXIV	Some Spectral Data of Various Perhalogenated Unsymmetrical Biaryls	70
Table XXV	List of New Compounds	73

SECTION I

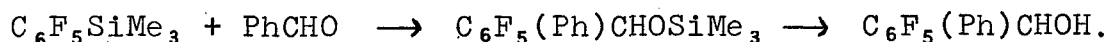
GENERAL INTRODUCTION

This report contains an account of two general aspects of our studies. One of them is concerned with polyhalogenated pyridines, and the other with polyhalogenated thiophenes. A major objective is to provide new or improved preparative procedures for types such as: $\text{CF}_3(\text{CF}_2)_n\text{-M}$ and $\text{M-(CF}_2)_n\text{-M}$.

We earlier showed that the di-metallic species were very probably formed intermediately in an in situ reaction of the following type:



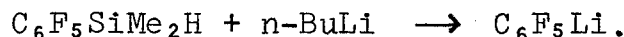
Quite satisfactory yields were obtained from the alpha,omega-dibromoperfluorinated alkane and where the metal used was either lithium or magnesium. This is significant because it by-passes the inordinately expensive alpha,omega-diiodoperfluorinated alkane. However, some orienting experiments indicated that the terminal C-SiMe_3 groups could not conveniently be converted to the desired C-M units. We then examined the possibility of developing conditions under which the C-SiMe_3 groups would behave like the versatile C-M units towards conventional substrates known to react with true organometallic compounds. For this purpose we considered it wise to first examine the closely related perhaloaryl types of the general formula R-SiMe_3 in which the R group is pentafluorophenyl, pentachlorophenyl, tetrachloro-4-pyridyl, etc. These did in fact react with a substrate such as benzaldehyde as follows:



In short, these perhaloaryl-trimethylsilanes behaved towards PhCHO exactly as a moderately reactive organometallic compound does. It is noteworthy that the simple non-halogenated PhSiMe_3 does not undergo such a reaction under corresponding conditions. This general reaction is being set aside for the time being because of the somewhat severe conditions required and because of the present limitations of reactive substrates, despite the satisfactory yields with a substrate such as PhCHO .

We soon observed in our studies involving mono- and di-organometallic derivatives of perchlorinated thiophenes (all of which we have shown to be preparable in high yields) that some very important and promising oblique approaches to the preparation of $\text{CF}_3(\text{CF}_2)_n\text{-M}$ and $\text{M-(CF}_2)_n\text{-M}$ types were possible.

For example, the perhaloaryldimethylsilanes react smoothly under extremely moderate conditions with n-butyllithium to give the perhaloaryllithium compound, as follows:



The yields are excellent. Again, it should be noted that the simple, non-halogenated compound, PhSiMe_2H , does not react in this manner to give PhLi . It is also noteworthy that the perhalogenated organolithium compounds formed in this reaction, proceed generally through a very smooth and neat transformation. For example, $(4\text{-C}_5\text{Cl}_4\text{N})\text{SiMe}_2\text{H}$ gives the $(4\text{-C}_5\text{Cl}_4\text{N})\text{Li}$ in the cleanest condition we have observed for any pyridyllithium.

It is a reasonable extension to expect that a compound such as $\text{HMe}_2\text{Si}-(\text{CF}_2)_n\text{-SiMe}_2\text{H}$ might give under uncommonly mild conditions the $\text{Li}-(\text{CF}_2)_n\text{-Li}$. Here the starting compound should be accessible via an in situ reaction described earlier for the preparation of $\text{Me}_3\text{Si}(\text{CF}_2)_n\text{SiMe}_3$, namely:



Another approach developed from the studies on the perchloro-thienylmetallic compounds is the marked effect of tertiary amines such as Et_3N on facilitating the halogen-metal exchange. Ordinarily, this exchange reaction occurs with great difficulty when the halogen is chlorine. The uncommon acceleration of this exchange when a complex of n-BuLi and a tertiary amine is used suggests that even the $\text{Cl}-(\text{CF}_2)_n\text{-Cl}$ type might be of promise in providing access to the $\text{M}-(\text{CF}_2)_n\text{-M}$ compounds. Obviously, these new approaches apply also to the mono-organometallic types: $\text{CF}_3(\text{CF}_2)_n\text{-M}$.

There are several approaches to obtaining perhalopyridines containing two functional groups such as $\text{HMe}_2\text{Si-}$. One is to start with a lesser number of halogens (such as the dibromo- or difluoropyridines) and derive from them by metalation and other procedures the polyhalo-dimetallic-pyridines. A number of these reactions are described in this report. It appears that more promising routes are to be expected if one starts with the perhalogenated pyridine, such as pentachloropyridine, and then replace (either directly or indirectly) two of the chlorine atoms by two useful $\text{HMe}_2\text{Si-}$ groups for polymer formation. Such studies are now underway. In all of this, it might be mentioned that perhalogenated heterocycles such as those of pyridine and thiophene have nuclei which in and of themselves are known to provide generally an extra measure of thermal stability, particularly in systems having no hydrogens attached directly to the nucleus.

SECTION II

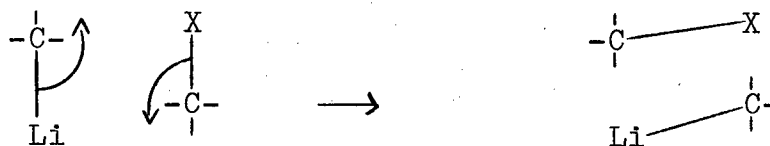
REACTIONS OF SOME POLYHALOPYRIDINES WITH ORGANOMETALLIC COMPOUNDS

1. INTRODUCTION

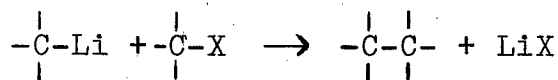
Pyridinoid types have greater thermal stability than homocycles. To make available some thermally stable compounds using nuclear halogenated pyridines, a continuation to our previous studies^{1,2,3,4,5} has led us to investigate some reactions of polyhalopyridines with organometallic compounds.

Previous studies in these laboratories^{6,7,8,9} and in other laboratories^{10,11,12,13} concerning the reaction of polyhalogenated pyridines with organolithium reagents have indicated the occurrence of the following basic reactions:

- (i) halogen-metal interconversion reaction^{14,6,7,8,9}, generally encountered for X = Cl or Br



- (ii) nucleophilic substitution reaction^{10,11,12,13}, particularly observed for X = F



- (iii) addition to the azomethine linkage^{7,8}.

The first reported example⁶ of a halogen-metal exchange reaction with pyridine was the formation of 3-pyridyllithium from 3-bromopyridine and *n*-butyllithium. The combination of low temperature and short reaction time kept to a minimum a number of competing side reactions such as addition to the azomethine linkage or coupling to form bipyridyl derivatives. The use of bulky organolithium reagents, for example *s*-butyllithium or *t*-butyllithium, did not help to reduce the amount of addition to the azomethine linkage^{7,8}.

It has been shown by Chambers, Drakesmith and Musgrave¹⁵ that hydrogen in 2,3,4,6-tetrafluoropyridine, 2,3,5,6-tetrafluoropyridine or in 2,4,6-trifluoropyridine is sufficiently acidic to afford pyridyllithiums using *n*-butyllithium. We now report related

metalation reactions with dihalopyridines and *n*-butyllithium. These reactions have a particular interest in view of the general statement in the review by Schofield¹⁵, "Metalation, the replacement of a nuclear hydrogen atom by a metal atom, as for example by lithium through the use of an alkyl lithium, is unknown in the pyridine series."

2. RESULTS AND DISCUSSION

Addition of *n*-butyllithium to an equimolar amount of 2,5-dichloropyridine in THF at -70°C gave a rapid metathetical reaction. This red-colored solution afforded an acid in 45% yield when poured over a slurry of solid carbon dioxide in ether. The neutralization equivalent of the acid by titration method was found to be 193. The calculated equivalent wt. 192, for 2,5-dichloropyridinecarboxylic acid indicated the occurrence of a metalation reaction. The NMR spectrum of the acid showed three singlets at -6.8 τ , 1.43 τ , and 2.03 τ , each integrating for one proton. But the NMR spectrum of the parent compound, 2,5-dichloropyridine, exhibited a doublet representing the 6-pyridyl proton, at 2.52 τ ($J_{64} = 2.8$ cps), two pairs of peaks centered at 3.24 τ ($J_{43} = 8.6$ cps), corresponding to the 4-pyridyl proton and a doublet at 3.51 τ ($J_{34} = 8.3$ cps), attributed to the 3-pyridyl proton. This clearly shows no coupling between 3-pyridyl and 6-pyridyl protons. The foregoing discussion suggests the structure of the acid to be 2,5-dichloro-4-pyridinecarboxylic acid. Thus, the intermediate lithium compound is established as 2,5-dichloro-4-pyridyllithium.

2,5-Dichloro-4-pyridyllithium was derivatized with chlorotrimethylsilane, dichlorodimethylsilane, benzaldehyde and benzophenone. The physical and spectral data of the compounds obtained are listed in Tables I, III and IV.

In a similar study, the reaction of 3,5-dichloropyridine with an equimolar amount of *n*-butyllithium in THF gave a mixture of intermediate lithium compounds. The derivatization of the pyridyllithium compounds with chlorotrimethylsilane afforded 3,5-dichloro-4-trimethylsilylpyridine in 56% yield, upon fractional distillation. The pot residue contained some, as yet, unidentified material. The structural assignment of the trimethylsilyl group is based on NMR studies of 3,5-dichloropyridine and 3,5-dichlorotrimethylsilylpyridine. In a like manner, it has been shown that metalation of 2,6-difluoropyridine takes place in the 3- position.

2,5-Dichloro-4-pyridylcopper was prepared by the reaction of the pyridyllithium compound with copper(I) halides. The intermediate copper compound afforded the acetyl or benzoyl derivative when reacted with acetyl or benzoyl chloride, respectively (Table II). However, the reaction with fumaryl chloride did not yield the expected dipyridyl diketone. Only 2,5,2',5'-tetrachloro-4,4'-bipyridyl was isolated in 4% yield. The identity of the bipyridyl compound was established through its superimposable IR and undepressed mixture melting point with an authentic sample. An authentic sample of the bipyridyl was obtained by the reaction of 2,5-dichloro-4-pyridyllithium* with an equimolar amount of copper (II) chloride.

Recently, pyridylmagnesium^{1 6} compounds have been prepared from halopyridines and phenylmagnesium bromide or iodide which involve halogen-metal exchange reactions. In a similar reaction, 2,5-dichloropyridine did not give the corresponding chloropyridylmagnesium halide, showing no evidence of halogen-metal interconversion. The recovery of unreacted 2,5-dichloropyridine was essentially quantitative (~90%).

In general, the yields of the compounds obtained (Tables I and II) were close to 40%; however, the yield of the intermediate lithium compound was 72.5% as established by a quantitative determination¹⁷. The low yields obtained may be attributed to the competing side reaction of 2,5-dichloro-4-pyridyllithium to give 6-chloro-3-pyridyne which in turn gives polymers. Trichloro-3-pyridyne¹⁸ has been reported to be formed by the elimination of lithium chloride from tetrachloro-4-pyridyllithium and trapped in the form of a 1,4-adduct with benzene.

Recently, it has been shown that the C-SiMe₃ unit in 2-trimethylsilylpyridine¹⁹ and in its perhaloaryl analogs²⁰ adds to benzaldehyde similar to C-M compounds. In a parallel reaction, 2,5-dichloro-4-trimethylsilylpyridine did not react with benzaldehyde under essentially identical conditions.

*Grignard reagents are known to give coupling products with copper(II) chloride, J. Krizewsky and E. Turner, J. Chem. Soc., 115, 559 (1919); see also H. Gilman and H. Parker, J. Amer. Chem. Soc., 46, 2823 (1924).

3. EXPERIMENTAL

All reactions were performed under a static pressure of dry oxygen-free nitrogen. Ethereal solvents were dried over sodium wire, excepting tetrahydrofuran, which was further distilled from lithium aluminium hydride. *n*-Butyllithium in hexane, was from Foote Mineral Co. Copper(I) iodide was obtained from Alfa Inorganic Chemicals. Copper(I) chloride was obtained by purification²¹ of a commercial sample. Organochlorosilanes were obtained from Dow-Corning Corporation and used after further purification by distillation.

IR spectra were determined as KBr pellets or thin films of pure liquid on sodium chloride plates, using a Perkin-Elmer Model 21 spectrophotometer. NMR spectra were recorded in carbon tetrachloride or deuterated chloroform, using a Varian A60 instrument. Mass spectra were obtained on an Atlas CH4. VPC analyses were carried out on an F & M Model 500 Gas Chromatograph using 4 ft. columns packed with Silicone Gum Rubber (15% on Chromosorb W) and D.C. Silicone oil 710 (15% on Chromosorb W).

a. Reaction of 2,5-dichloropyridine with *n*-butyllithium and subsequent reaction with derivatizing reagents

A solution of *n*-butyllithium (*x* mole) in hexane was added dropwise (2 drops/sec.) with stirring, to the solution of 2,5-dichloropyridine (*x* mole) in THF or in ether at -70°C. After nearly 3 hr. of stirring Color Test II²² was negative and Color Test I²² positive. Several preparations were made on a 0.05 or 0.10 mole scale with 1.2 l. of solvent used per mole of 2,5-dichloropyridine.

(1) Reaction of 2,5-dichloropyridyllithium with solid carbon dioxide

The reaction mixture was poured over a slurry of solid carbon dioxide and ether. The reaction mixture was allowed to come to room temperature, hydrolyzed with dil. HCl and extracted with ether. The ether layer was dried (anhydrous Na₂SO₄) and the solvent was removed to obtain the corresponding acid. Sublimation of this acid and recrystallization (EtOH) gave 4.0 g. (43%) m.p. 223°C, decomp.

(2) Reaction of 2,5-dichloropyridyllithium with chlorosilanes

The appropriate chlorosilane (*x* mole) was added dropwise to the pyridyllithium (*x* mole) in THF or in ether at -70°C. The resulting reaction mixture was stirred until Color Test I²² was negative. The reaction was warmed to room temperature and the solvent was removed under reduced pressure. The dark brown residue

was taken up in petroleum ether (b.p. 60-70°C). The hexane extract was separated from the inorganic salt by filtration and chromatographed over neutral alumina to separate the corresponding 2,5-dichloro-silylpyridines.

(3) Reaction of 2,5-dichloropyridyllithium with carbonyl compounds

A solution of the carbonyl compound (0.10 mole) in dry THF (30 ml.) was added dropwise to 2,5-dichloropyridyllithium (0.10 mole) in THF at -70°C. The reaction mixture was stirred until Color Test I²² became negative. It was allowed to warm to room temperature and worked up in the usual way (hydrolyzed with 6N HCl, extracted with ether or ether-benzene mixture, dried over anhydrous sodium sulfate and the solvent stripped off).

(4) Reaction of 2,5-dichloropyridyllithium with copper (I) halides in appropriate solvents, and subsequent treatment with acid chlorides

To the solution of 2,5-dichloropyridyllithium (0.10 mole) in 120 ml. of THF or in ether at -70°C was added an appropriate copper(I) halide (0.10 mole) (dried in an oven at 120-130°C and cooled in the desiccator over CaSO₄) in one lot. Color Test I²² of the mixture was negative in 12-15 hr., however, the mixture was normally stirred additionally for 4-5 hr. at -70°C so as to ensure the complete formation of the copper compound. To the copper compound (0.10 mole) so obtained by following the Method A²³, was added an acid chloride (0.10 mole) and the mixture was stirred for several hours (Table II). Copper salts were removed by the extraction with saturated aqueous ammonium chloride (50%) and conc. ammonium hydroxide (50%). The mixture was extracted into ether, dried over anhydrous sodium sulfate and stripped of the solvent. The crude material was dissolved in 1:1 ether - C₆H₆ and placed on a silica gel column. Elution with petroleum ether (b.p. 60-70°C) gave the purified ketone.

b. Preparation of 2,5,2',5'-tetrachloro-4,4'-bipyridyl

Copper(II) chloride (0.05 mole) was added to 2,5-dichloropyridyllithium (0.05 mole) in THF at -70°C and stirred until Color Test I²² was negative (6-8 hr.). The reaction mixture was hydrolyzed, extracted with ether, dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. Column chromatography over silica afforded 2.75 g. (36%) of 2,5,2',5'-tetrachloro-4,4'-bipyridyl, m.p. 121-2°C.

c. Reaction of 2,5-dichloropyridine with phenylmagnesium bromide

Phenylmagnesium bromide (0.05 mole) in ether was slowly added to a solution of 2,5-dichloropyridine (7.4 g., 0.05 mole) in THF (50 ml.). After stirring for 6 hr., Color Test I²² was positive. The solution was poured over a slurry of solid carbon dioxide and ether. The work-up of the reaction gave 6.0 g. of benzoic acid, m.p. and mixture m.p. 121-2°C, and 6.8 g. of 2,5-dichloropyridine (recovery ~90%). This shows no evidence of halogen-metal exchange reaction¹⁶.

d. Reaction of 3,5-dichloropyridine with n-butyllithium and subsequent reaction with chlorotrimethylsilane

To a stirred solution of 3,5-dichloropyridine (7.4 g., 0.05 mole) in THF (120 ml.) at -70°C was added dropwise n-butyllithium (31.25 ml., 0.05 mole) in hexane. After stirring for nearly 2 hr., following the complete addition of n-butyllithium, Color Test I²² was positive and Color Test II negative. Chlorotrimethylsilane (5.4 g., 0.05 mole) was added dropwise and the reaction mixture was stirred for 4 hr. so as to make sure that the reaction was complete even though Color Test I was negative within 20 min. The reaction was worked up under anhydrous conditions (as in a.; (2)) to give a crude reaction mixture. The fractional distillation of this gave 3,5-dichloro-4-trimethylsilylpyridine (4.4 g., ~56%), b.p. 60-65°C/0.15 mm.

IR and NMR data of the compound are as follows:

IR: 3075, 2945, 2879 (C-H); 1552, 1500, 1492, 1428 (substituted pyridine ring stretching vibrations); 1248, 850, 759 (SiMe₃); 809 (C-Cl).

NMR: 1.67 τ (S), 2-H and 6-H (pyridyl); 9.52 τ (S), SiMe₃.

The pot residue (4.8 g.) contained three compounds (VPC) the identity of which have not yet been established.

e. Metalation of 2,6-difluoropyridine with n-butyllithium

(1) In THF: 1:1 ratio of n-BuLi + 2,6-C₅F₂H₃N

To a 250 ml. 3-necked flask was added 60 ml. THF and 1.15 g. (0.01 mole) of 2,6-C₅F₂H₃N. The mixture was cooled to -70°C and n-BuLi (0.01 mole) was added during 10 min. After 2.5 hr., a small sample was withdrawn and reacted with excess Me₃SiCl. VPC showed a substantial amount of a material of longer retention time than 2,6-C₅F₂H₃N. The reaction was stirred for an additional

1 hr. and treated with 0.012 mole of Me_3SiCl (20% excess) and stirred for 3 hr. while warming to room temperature. Hydrolysis with 3N HCl and the usual work-up (as in a. (3)) gave 1.2 g. of an oil b.p. $74-76^\circ\text{C}/16$ mm.

IR: (Cm^{-1}) 3105 VW; 2950 M, 2880 W, 1587 S, 1575 Sh, 1455 S, 1370 S, 1280 S, 1265 S, 1250 S, 1210 W, 1120 M, 1067 S, 994 S, ~840 S(VB), 770 M, 755 W, 738 M.

NMR: quartet centered at 2.13 τ
multiplet at 3.28 τ
singlet at 9.69 τ
area ratio is 1:1:9, respectively.

The material is 3-trimethylsilyl-2,6-difluoropyridine on the basis of its NMR spectrum. In a separate reaction, carbonation of the aryllithium gave an acid, 1.11 g. (70%) m.p. $162-70^\circ\text{C}$ with decomposition.

(2) In THF: 2:1 ratio of $n\text{-BuLi}$ to $2,6\text{-C}_5\text{F}_2\text{H}_3\text{N}$

Under the same conditions as in (a.), the 2,6-difluoropyridine in THF was reacted with two equivalents of $n\text{-BuLi}$. After a total of 26 hr., only the monolithio- derivative was in evidence. (By VPC after treating with Me_3SiCl).

(3) In Ether: 1:1 ratio of $n\text{-BuLi}$ to $2,6\text{-C}_5\text{F}_2\text{H}_3\text{N}$

To 1.15 g. (0.01 mole) of 2,6-difluoropyridine in 60 ml. ether at -70°C was added 0.01 mole of $n\text{-BuLi}$. After 3 hr., Color Test I was positive and Color Test II was negative. The mixture was derivatized with Me_3SiCl (0.012 mole) and stirred overnight. VPC showed that the mixture contained ~1% of 3-trimethylsilyl-2,6-difluoropyridine and another material of longer retention time. This oil had a complex NMR spectrum and has not as yet been identified. It does not appear to be 4-trimethylsilyl-2,6-difluoropyridine and may therefore be a ring cleavage product. In a separate reaction, carbonation of the mixture gave the same material as had been isolated by treatment with Me_3SiCl indicating that the reaction in ether is other than metalation but may be a ring opening or possibly an alkylation type reaction.

All the compounds were characterized by analytical and physical methods. Some of the properties and spectral data of the new compounds are described in Tables I, II, III and IV.

Table I. Reactions of 2,5-Dichloro-4-pyridyllithium with Some Derivatizing Reagents at -70°C

Derivatizing Reagent	Solvent	Product	Time ^a (h)	Yield (%)	m.p. ($^{\circ}\text{C}$)	b.p. ($^{\circ}\text{C}$)
CO_2	THF	4-COOH($\text{C}_5\text{H}_2\text{Cl}_2\text{N}$)	2-3	41	222-23 $^{\circ}$	
ClSiMe_3	THF	4-Me ₃ Si($\text{C}_5\text{H}_2\text{Cl}_2\text{N}$) ^b	2	41	46-47 $^{\circ}$ (hexane)	83 $^{\circ}$ /1.5 mm
ClSiMe_3	Ether	4-Me ₃ Si($\text{C}_5\text{H}_2\text{Cl}_2\text{N}$) ^b	10-12	5-7 ^c		
Cl_2SiMe_2	THF	(4- $\text{C}_5\text{H}_2\text{Cl}_2\text{N}$) ₂ SiMe ₂ ^b	2-3	39	107.5 -108 $^{\circ}$ (hexane)	
$\text{C}_6\text{H}_5\text{CHO}$	THF	$\text{C}_6\text{H}_5\text{CH}(\text{OH})-4-(\text{C}_5\text{H}_2\text{Cl}_2\text{N})$ ^d	5-7	39.3	169-70 $^{\circ}$ ($\text{C}_2\text{H}_5\text{OH}$)	
(C_6H_5) ₂ CO	THF	(C_6H_5) ₂ C(OH)-4-($\text{C}_5\text{H}_2\text{Cl}_2\text{N}$) ^d	5-7	41	128-29 $^{\circ}$ ($\text{C}_2\text{H}_5\text{OH}$)	

^a Stirring time after the complete addition of derivatizing agent, usually 1-2 h more after Color Test I²² was negative.

^b The products were isolated by working up under essentially anhydrous conditions; for detailed procedure, refer to the experimental section.

^c Yield by VPC. VPC of the crude product exhibited a complex VPC chromatogram showing 8 peaks.

^d Worked up using ether-benzene mixture.

Table II. Reactions of 2,5-Dichloro-4-pyridylcopper^a with Some Acid Chlorides at -70°C

Copper Halide	Acid Chloride	Product	Solvent	Time ^b	Yield (%)	m.p. (°C)	b.p. (°C)
CuI	C ₆ H ₅ COCl	4-C ₆ H ₅ CO(C ₅ H ₂ Cl ₂ N)	THF	8	30	130-31° (hexane)	86-87°/ 0.75mm
CuI	CH ₃ COCl	4-CH ₃ CO(C ₅ H ₂ Cl ₂ N)	THF	8	29		
CuI	C ₆ H ₅ COCl	4-C ₆ H ₅ CO(C ₅ H ₂ Cl ₂ N)	Ether	16-18	10-15 ^c		
CuI	CH ₃ COCl	4-CH ₃ CO(C ₅ H ₂ Cl ₂ N)	Ether	16-18	8-10 ^c		
CuCl	C ₆ H ₅ COCl	4-C ₆ H ₅ CO(C ₅ H ₂ Cl ₂ N)	THF	8-10	16	130-31° (hexane)	
CuCl	CH ₃ COCl	4-CH ₃ CO(C ₅ H ₂ Cl ₂ N)	THF	8-10	18		84-85°/ 0.70mm
CuI	ClCOCH:CHCOCl	(4-C ₅ H ₂ Cl ₂ N) ₂ ^d	THF	16-18	4	121.5-22° (hexane-benzene)	

^a Prepared by following Method A³. After the addition of copper(I) halide, the reaction mixture was stirred until Color Test I²² was negative (usually 12-15 hr.).

^b Stirring time after the complete addition of acid chloride.

^c Yield by VPC. The crude product showed a complex VPC chromatogram.

^d Authentic sample was prepared from 2,5-dichloro-4-pyridyllithium and Cu(II)Cl. Refer to the experimental section for details.

Table III. Spectroscopic Data of Various Compounds

Compounds	IR ^a (cm ⁻¹)	NMR ^b (τ)	M. Spec. ^c
RCOOH ^d	3080 (C-H); 2735 (O-H, dimeric); 1715 (C=O, dimeric); 1585, 1537, 1467, 1436 (substituted pyridine ring stretching vibrations); 789 (C-Cl).	-6.8 (s), (COOH); 1.43 (s), 6-H (Pyridyl); 2.03 (s), 3-H(Pyridyl).	191, 193 (molecule ions with the correct intensity ratio for a molecule containing two Cl atoms, calcd. 191.90 taking Cl=35.45); 174, 176 (loss of -OH); 146, 148 (loss of -COOH); 45 (-COOH).
RSiMe ₃	3078, 2962, 2879 (C-H); 1555, 1504, 1488, 1429 (substituted pyridine ring stretching vibrations); 1245, 844, 761 (SiMe ₃); 803 (C-Cl).	1.79 (s), 6-H (pyridyl); 2.78 (s), 3-H (pyridyl); 9.63 (s), Si-Me ₃ .	219, 221 (molecule ions with the correct intensity ratio for a molecule containing two Cl atoms, calcd. 219.90 taking Cl=35.45); 204, 206 (loss of -CH ₃); 168, 170 (loss of -CH ₃ and Cl); 73 (-SiMe ₃).
R ₂ SiMe ₂	3036, 2947 (C-H); 1564, 1505, 1455, 1439 (substituted pyridine ring stretching vibrations); 1253, 853, 803 (SiMe ₂); 793 (C-Cl).	1.73 (s), 6-H (pyridyl); 2.73 (s), 3-H (pyridyl); 9.24 (s), Si-Me ₂ .	350, 352, 354, 356, 358 (molecule ions with the correct intensity ratio for a molecule containing four Cl atoms, calcd. 351.8 taking Cl=35.45); showed mass spectral fragmentation peaks with the expected intensity ratio corresponding to the loss of -CH ₃ , -CH ₃ and Cl.

Table III. (Contd.)

Compound	IR ^a (cm ⁻¹)	NMR ^b (τ)	M. Spec. ^c
RCH(OH)C ₆ H ₅	3240 (O-H); 3084, 2876, (C-H); 1615, 1571, 1528, 1484, 1453 (benzene and substituted pyridine ring stretching vibrations); 813 (C-Cl).	1.78 (s), 6-H (pyridyl); 2.28 (s), O-H; 2.28 (s), (phenyl); 2.78 (s), 3-H (pyridyl); 3.97 (s), C-H. Q	253, 255 (molecule ions with the correct intensity ratio for a molecule containing two Cl atoms, calcd. 253.90 taking Cl=35.45); mass spectral peaks with the correct intensity ratio corresponding to the loss of H ₂ O, -Cl, -C ₅ H ₂ Cl ₂ N, and -C ₆ H ₅ ; 77 (-C ₆ H ₅).
RC(OH)(C ₆ H ₅) ₂	3279 (O-H); 3030 (C-H); 1597, 1572, 1524, 1493, 1443 (benzene and substituted pyridine ring stretching vibrations); 800 (C-Cl).	1.73 (s) ^e , 6-H (pyridyl); 2.70 (m), (phenyl); 3.20 (s), 3-H (pyridyl); 6.08 (s), C O H.	329, 331 (molecule ions with the correct intensity ratio for a molecule containing two Cl atoms, calcd. 329.90 taking Cl=35.45); mass spectral peaks corresponding to the loss of -Cl, -C ₆ H ₅ , and -C ₅ H ₂ Cl ₂ N, with the expected intensity ratio; 77 (-C ₆ H ₅).
RCOC ₆ H ₅	3077, 3030, 2985 (C-H); 1667 (C=O); 1592, 1580, 1570, 1527, 1445 (benzene and substituted pyridine ring stretching vibrations); 798 (C-Cl).	1.48 (s), 6-H (pyridyl); 2.33 (m), (phenyl); 2.67 (s), 3-H (pyridyl).	251, 253 (molecule ions with the correct intensity ratio for a molecule containing two Cl atoms, calcd. 251.90 taking Cl=35.45); mass spectral peaks with the correct intensity ratio corresponding to the loss of -C ₆ H ₅ CO, and -C ₅ H ₂ Cl ₂ NCO.

Table III. (Contd.)

Compound	IR ^a (cm ⁻¹)	NMR ^b (τ)	M. Spec. ^c
RCOCH ₃	3077, 2941 (C-H); 1742, 1709, (C=O); 1570, 1538, 1527, 1445 (substituted pyridine ring stretching vibra- tions); 798 (C-Cl).	1.55 (s), 6-H (py- ridyl); 2.45 (s), 3-H (pyridyl); 7.28 (s), OC-CH ₃ .	189, 191 (molecule ions with the correct intensity ratio for a molecule con- taining two Cl atoms); mass spectral peaks with the correct intensity ratio corresponding to the loss of -CH ₃ , -CH ₃ CO, and -C ₅ H ₂ Cl ₂ NCO).
R-R	3049 (C-H); 1563, 1522, 1464, 1433 (substituted py- ridine ring stretch- ing vibrations); 777 (C-Cl).	1.47 (s), 6 and 6'-H (pyridyl); 2.78 (s), 3 and 3'-H (pyridyl).	292, 294, 296, 298, 300 (molecule ions with the correct intensity ratio for a mol- ecule containing four Cl atoms, calcd. 293.80 taking Cl=35.45); mass spectral peaks with the correct in- tensity ratio corresponding to the loss of one Cl atom.
R ₂ CO	3030, 2899 (C-H); 1658 (C=O); 1563, 1550, 1481, 1449 (substituted py- ridine ring stretch- ing vibrations); 819. 809 (C-Cl).	f -----	320, 322, 324, 326, 328 (mol- ecule ions with the correct intensity ratio for a mol- ecule containing four Cl atoms, calcd. 321.80 taking Cl=35.45); mass spectral peaks with the correct in- tensity ratio corresponding to the loss of one Cl atom, CO molecule and one Cl and CO; 146, 148 (-C ₅ H ₂ Cl ₂ N)..

Table III. (Contd.)

<u>a</u>	R = 4-C ₅ H ₂ Cl ₂ N-
<u>b</u>	s = singlet, m = multiplet.
<u>c</u>	The number of chlorine atoms present in each compound was conclusively proved from the "isotopic cluster" produced in the spectrum; (Fred W. Mc Lafferty, "Interpretation of Mass Spectra", W. A. Benjamin, Inc., New York (1967) P. 22.
<u>d</u>	NMR spectrum was recorded in C ₅ D ₅ N.
<u>e</u>	Broad singlet.
<u>f</u>	Much less soluble in CCl ₄ and CDCl ₃ .

Table IV. Analyses of Various Compounds

Compound	% Chlorine	
	Calculated	Found
4-COOH(C ₅ H ₂ Cl ₂ N) ^a	36.94	
4-Me ₃ Si(C ₅ H ₂ Cl ₂ N) ^b	32.24	
(4-C ₅ H ₂ Cl ₂ N) ₂ SiMe ₂ ^c	40.30	
C ₆ H ₅ CH(OH)-4-(C ₅ H ₂ Cl ₂ N)	27.88	27.64
(C ₆ H ₅) ₂ C(OH)-4-(C ₅ H ₂ Cl ₂ N)	21.19	21.36
4-C ₆ H ₅ CO(C ₅ H ₂ Cl ₂ N)	28.14	27.90
4-CH ₃ CO(C ₅ H ₂ Cl ₂ N)	37.33	
(4-C ₅ H ₂ Cl ₂ N) ₂ ^d	48.26	47.56

^a Neutral Equivalent: Calc., 192; Found, 193.

^b Si: Calc., 12.73; Found, 12.55.

^c Si: Calc., 7.95; Found, 7.40.

^d 98-99% pure by VPC.

SECTION III

TRICHLORO-2-THIENYLMAGNESIUM HALIDE

1. INTRODUCTION AND DISCUSSION

In continuation of our studies concerning the preparation and reactions of polyhaloorganometallic compounds^{1,2,23,24}, we have prepared trichloro-2-thienylmagnesium halide in 98% yield.

Prior to this work a few reports appeared concerning the preparation of trichloro-2-thienylmagnesium halide. Steinkopf and co-workers^{25,26} were the first to prepare trichloro-2-thienyl magnesium halide from tetrachlorothiophene by the entrainment technique²⁷. They used two equivalents of the entrainer, and diethyl ether as the solvent. When methyl iodide²⁵ was used as the entrainer the yield of the 2,3,4-trichlorothiophene subsequent to hydrolysis of the Grignard reagent was 46%; whereas the yield was 18% when ethyl bromide²⁶ was the entraining agent. Later Bachman and Heisey²⁸, without giving experimental details, reported that the conversion of tetrachlorothiophene to trichloro-2-thienylmagnesium halide in the presence of the "cohalide" (C_2H_5Br) "proceeded less satisfactorily" than the conversion to trichloro-2-thienyllithium by *n*-butyllithium. In other studies, we have confirmed their ready formation of trichloro-2-thienyllithium. Recently, Rausch and co-workers²⁹ have mentioned the formation of trichloro-2-thienylmagnesium halide, but experimental details were not provided. We have found that trichloro-2-thienylmagnesium halide can be prepared in THF in 98% yield from tetrachlorothiophene and magnesium using one equivalent of ethylene bromide as the entrainer.

The trichloro-2-thienylmagnesium halide has been prepared in THF by three methods: (1) from tetrachlorothiophene, magnesium and ethylene bromide (as entrainer); (2) from tetrachlorothiophene and various copper-magnesium alloys³⁰ in the presence of a catalytic amount of iodine; and (3) from tetrachlorothiophene and magnesium with or without various catalysts, (such as iodine, activated copper-magnesium alloy (10.2%)³¹ ethylene bromide, etc.). Of the three methods the last is the most unsatisfactory in view of the poor yield of the Grignard reagent and the unusually long reaction time. The first method, which involves ethylene bromide as the entrainer, is the preferred one because of the short reaction time and the high yield (98%).

When ethylene bromide (*x* moles) was used as the entrainer, tetrachlorothiophene (*x* moles) reacted with magnesium (2*x* g. at.) in THF (130 ml.) to give, after hydrolysis, 2,3,4-trichlorothiophene in 97% yield. The trichloro-2-thienylmagnesium halide gives

after carbonation, trichloro-2-thiophenecarboxylic acid (87%). When a half-equivalent of the entrainer was used in the above reaction the yield of 2,3,4-trichlorothiophene, subsequent to hydrolysis of an aliquot, was 77% immediately after the addition (2 1/2 hr.) of the entrainer was complete. However, when the reaction mixture was stirred for an additional 20 hr. at room temperature the yield rose to 98%, and subsequent carbonation afforded the corresponding carboxylic acid in 87% yield. The yield of trichloro-2-thienylmagnesium halide was sensitive to the amount of THF used. Thus under similar conditions, the yield of 2,3,4-trichlorothiophene after hydrolysis of the Grignard reagent was 97% when 130 ml. THF was used, but 55-60% when 60 ml. was used. The low yield in the latter case is probably attributable to the protective action of the precipitated magnesium bromide - THF complex. This observation is supported by the fact that when enough THF was added to dissolve the insoluble complex, the reaction went to near completion to give 97% of 2,3,4-trichlorothiophene after hydrolysis. That the insoluble magnesium halide - THF complex retards the formation of a Grignard reagent was also observed by Tamborski and co-workers³² in their studies starting with hexafluorobenzene.

In addition to THF, we investigated diethyl ether and 2,2,4,4-tetramethyltetrahydrofuran (TM-THF) as solvents. Diethyl ether was much inferior to THF as a solvent for the preparation of this Grignard reagent. In ether, with one equivalent of the entrainer ($C_2H_4Br_2$), the yield of 2,3,4-trichlorothiophene, after hydrolysis, was 14-18%. The low solubility of the Grignard reagent in ether may, in part, be responsible for the poor yield. No detectable amount of trichloro-2-thienylmagnesium halide was formed in TM-THF alone. One of the important roles a solvent plays in the formation of a Grignard reagent is the formation of a soluble complex with the reagent. This keeps the surface of magnesium metal clean or active. If this complex formation is restricted by some factors such as steric hindrance then the Grignard reagent formation would be retarded. Failure to detect even a small amount of the trichloro-2-thienyl Grignard reagent in TM-THF may be partly due to the steric hindrance encountered by this solvent to form a complex with the Grignard reagent. A similar explanation has been given for the poor solvent character of 2,5-dimethyl-THF and 2,2,5,5-tetramethyl-THF in the preparation of arylmagnesium halides³³.

In the presence of a catalytic amount of iodine, tetrachlorothiophene (x moles) reacted with copper-magnesium alloys³⁰

(x g. at. of Mg) in THF to give high yields (82-96%) of trichloro-2-thienylmagnesium chloride. Of the various copper-magnesium alloys, we tried those containing 10.2, 18.9, 30 and 39% copper. The copper-magnesium alloy containing 39% copper appeared to be the most effective because the time required for a complete conversion of the tetrachlorothiophene to trichloro-2-thienylmagnesium chloride was 8 hr. as compared with 13-14 hr. required by the others. Furthermore, the induction period in this case was the shortest. The copper-magnesium alloy containing 10.2% copper gave a few per cent higher yield of the Grignard reagent. This alloy, which has a low copper content, always gave a clean reaction mixture.

Our attempts to prepare trichloro-2-thienylmagnesium chloride from tetrachlorothiophene and magnesium in the presence of small amount of various catalysts or without any catalyst were not very rewarding. Tetrachlorothiophene alone reacted with Grignard grade magnesium in THF over a period of 2 weeks to give, after hydrolysis, 2,3,4-trichlorothiophene in 45% yield. Tetrachlorothiophene, however, reacted faster with magnesium when the reaction was initiated by means of a catalyst such as 10.2% copper-magnesium alloy activated with iodine³¹, ethylene bromide or iodine and copper-magnesium alloy (39%). Of the three catalysts tried, ethylene bromide appeared to be the most efficient (Table VII).

Like hexachlorobenzene³⁴, tetrachlorothiophene did not form a di-Grignard reagent to any significant extent. When ethylene bromide (0.1 mole) was used with a long addition time (7 hr.), tetrachlorothiophene (0.05 mole) reacted with magnesium (0.15 g. at.) in THF (130 ml.) to give after hydrolysis 2,3,4-trichlorothiophene (88-90%) and 3,4-dichlorothiophene (4-7%). The 3,4-dichlorothiophene in this experiment might have originated from the hydrolysis of the corresponding di-Grignard reagent. The use of two equivalents of a copper-magnesium alloy (30% or 39%) in THF, either at room temperature or at the refluxing temperature of THF, did not produce a di-Grignard reagent to any detectable extent.

Trichloro-2-thienylmagnesium halide is only moderately stable at room temperature. A THF solution of the reagent stirred at the ambient temperature (ca. 27°C) for 5 1/2 days showed a decrease of 49% in the yield of trichloro-2-thienyltrimethyl silane. Similarly, trichloro-2-thienylmagnesium halide refluxed in THF for 4 days gave, subsequent to carbonation, the corresponding carboxylic acid in 38% yield. In this connection it may be mentioned that the trichloro-2-thienyllithium has been found to be stable^{29,35} for days in a number of solvents such as ether, hexane, etc.

The trichloro-2-thienylmagnesium halide reacted in a conventional fashion with a number of metal halides and organic reagents. We have prepared several 2-silyltrichlorothiophenes in THF by in situ reactions between tetrachlorothiophene, a copper-magnesium alloy (or magnesium turnings in the presence of a few drops of ethylene bromide) and an appropriately substituted chlorosilane. These one-step as against the conventional two-step reactions have the advantages of requiring less attention once initiated, and their reaction time can be short^{3 6}. One of the analytical procedures for RMgX was the conventional acid titration^{3 7}.

2. EXPERIMENTAL

The reactions were carried out under a positive pressure of dry, oxygen-free nitrogen. The ethereal solvents were dried over sodium-wire and distilled prior to use from sodium-benzophenone ketyl. Magnesium turnings were from the Mallinckrodt Chemical Works. Tetrachlorothiophene was obtained commercially and used without further purification. The VPC analyses were carried out by an F and M Model 500 Gas Chromatograph using a 4 ft. column packed with 15% Silicone Gum Rubber on Chromosorb W (60-80 mesh). For quantitative VPC analyses durene was used as the internal standard. The yields were computed on the starting amount of tetrachlorothiophene. All temperatures quoted are uncorrected.

a. Preparation of trichloro-2-thienylmagnesium halide

(1) From tetrachlorothiophene and magnesium by the entrainment technique (A recommended general procedure)

Tetrachlorothiophene (11.1 g., 0.05 mole), magnesium (2.4 g., 0.1 g. at.) and THF (10-15 ml.) were placed in a three-necked flask which was previously flushed with dry nitrogen. A solution (10 ml.) prepared by dissolving ethylene bromide (9.4 g., 0.05 mole) in THF (140 ml.) was added and the mixture stirred at the ambient temperature. A reddish brown color developed, changed to yellowish and then to a dirty grey color within 30 seconds. The exothermic reaction was moderated with an iced-water bath after the dropwise addition of the rest of the ethylene bromide had been started. After the addition (2 hr.), durene (internal standard, 4.0927 g.) was added to the resulting dark brown Grignard solution. A VPC study of an hydrolyzed aliquot indicated the presence of 2,3,4-trichlorothiophene in 97% yield. For yields of this order, it was sometimes necessary to stir the reaction mixture for a few hours after the addition of the entrainer. The trichloro-2-thienylmagnesium halide gave a strong Color Test I^{2 2}. The Grignard reagent could be detected when the solution was approximately 0.065N, although the color developed rather slowly.

The trichloro-2-thienyl Grignard reagent prepared as above was carbonated at 0°C by bubbling in dry carbon dioxide. The reaction mixture was hydrolyzed (3N HCl, 100 ml.) and 100 ml. of petroleum ether added. The organic layer was separated and the acid products extracted into an aqueous Na₂CO₃ solution (three portions of 100 ml. each). The aqueous solution was then acidified (HCl) and extracted with three-100 ml. portions of ether. Evaporation of the ether and subsequent recrystallization from chloroform gave trichloro-2-thiophenecarboxylic acid (10.0 g., 87%), m.p. 226.5-227°C [cited²⁵: 224°C], mixed m.p. with a sample³⁵ prepared by the carbonation of the corresponding lithium reagent was undepressed. Table V shows the effect of various solvents and the amount of the entrainer on the yield of trichloro-2-thienylmagnesium halide.

(2) From tetrachlorothiophene and copper-magnesium alloy

A mixture of tetrachlorothiophene (11.1 g., 0.05 mole), copper-magnesium alloy (containing 39% copper) (0.05 g. at. of Mg), iodine (0.6 g.) and THF (120 ml.) was stirred at the ambient temperature (using a water bath). Within 1/2 hr. Color Test I²² was positive. The reaction was complete within 8 hr. (VPC studies). Acid titration³⁷ of an hydrolyzed aliquot revealed a yield of 89%. The Grignard reagent was then carbonated as before to give trichloro-2-thiophenecarboxylic acid (8.8 g., 76%), m.p. 226-227°C. In a similar manner, a number of magnesium alloys with different copper content were tried. Table VI summarizes the yields of trichloro-2-thienylmagnesium chloride by this procedure.

(3) From tetrachlorothiophene and magnesium in the presence of various catalysts

The general procedure involved in these reactions was to stir at the ambient temperature a mixture of a small amount (0.5 g.) of a catalyst, magnesium (x g. at.) and a few ml. of a solution of tetrachlorothiophene (x mole) in THF (~120 ml.). When the reaction had started as evidenced by the change of color and a positive Color Test I, the rest of the tetrachlorothiophene in THF was added slowly and the mixture was stirred at the ambient temperature. Table VII shows the yields obtained by this method.

b. Attempted preparation of a di-Grignard reagent from tetrachlorothiophene

(1) By the entrainment technique

This experiment was similar to the preparation of trichloro-2-thienylmagnesium halide from tetrachlorothiophene and magnesium by the entrainment technique, the only exceptions were the use of two equivalents of the entrainer and three equivalents of magnesium.

The addition of the entrainer took 7 hr. and the mixture was stirred at room temperature for 24 hr. VPC of an hydrolyzed aliquot indicated the presence of 3,4-dichlorothiophene (4-7%) and 3,4,5-trichlorothiophene (88-90%).

(2) Use of copper-magnesium alloy

A mixture of tetrachlorothiophene (x moles), iodine (0.5 g.) and copper-magnesium alloy (either 30% or 39% copper) (2x g. at. of Mg) in THF (120 ml.) stirred either at room temperature for 16 hr. or at the refluxing temperature for 5 hr. did not produce a di-Grignard reagent in detectable amounts.

c. Stability of trichloro-2-thienylmagnesium halide in THF

Trichloro-2-thienylmagnesium halide was prepared from tetrachlorothiophene (0.05 mole), magnesium (0.10 g. at.) and ethylene bromide (0.05 mole) in THF. The resulting reagent was stirred under dry nitrogen at room temperature. The yield was determined by VPC of aliquots treated with Me_3SiCl ($n\text{-C}_{16}\text{H}_{34}$ was the internal standard). The yield fell from an initial 85% to 36% during 132 hr.

In a separate experiment, the Grignard reagent was refluxed for 4 days in THF and the resulting dark brown reaction mixture was carbonated to yield trichloro-2-thiophenecarboxylic acid (38%), m.p. 226-227°C (identified by mixed m.p.).

d. Reactions of trichloro-2-thienylmagnesium halide with metal halides and miscellaneous reagents

The general procedure for these reactions consisted of two steps. The first involved the preparation of the Grignard reagent from tetrachlorothiophene (0.05 mole), magnesium (0.1 g. at.) and ethylene bromide (0.05 mole) in THF (150 ml.). The second consisted of the addition of an appropriate reactant (0.05 mole) to the Grignard reagent. Table VIII represents the various experimental conditions along with the yields and m.p. of the different products.

e. In situ preparation of various 2-silyltrichlorothiophenes

The general procedure was to stir a mixture of tetrachlorothiophene (x moles), a substituted chlorosilane (1.1 x moles) and an appropriate copper-magnesium alloy (x g. at. of Mg) in THF (100 ml.) for at least 10 hr. A water bath was used to moderate the reactions. Table IX summarizes these reactions. The various products were identified by VPC and IR spectra.

Table V. The effect of solvent and the amount of entrainer on the yield of the tri-chloro-2-thienylmagnesium halide

C ₄ Cl ₄ S (mole)	Mg (g.at.)	C ₂ H ₄ Br ₂ (mole)	Solvent (ml.)	Time of addition of the entrainer (hr.)	Induction period ^a (min.)	Reaction time ^b after the addition (hr.)	Yield of C ₄ Cl ₃ HS of the acid ^c (%) ^d	Yield of the acid ^c (%) ^d	Unreacted C ₄ Cl ₄ S (%) ^d
0.05	0.10	0.05	THF (130)	2	<1	0	97	87 (10g.)	---
0.05	0.75	0.025	THF (130)	2½	<1	0	77	---	22
						20	98	87 (10g.)	3
0.05	0.10	0.05	THF (60)	2	<1	0	55-60	---	---
						20	97	---	---
0.025	0.05	0.025	Ether (50)	1¼	4-5	0	14-18	---	82-85
0.05	0.10	0.05	TM THF (130)	1½	---	0	---	---	100
						10	---	---	100

^a This was an approximate time required for a positive response to Color Test I²² after ca. 10 ml. of the ethylene bromide solution had been added and the mixture stirred at the ambient temperature.

^b Reaction time after the addition of the entrainer.

^c Estimated by VPC using durene as internal standard.

^d Based on the amount of tetrachlorothiophene.

^e 2,2,4,4-tetramethyltetrahydrofuran (b.p. 121°C) (TM THF).

Table VI. Trichloro-2-thienylmagnesium chloride from tetrachlorothiophene and various copper-magnesium alloys^a

Copper content % (g.at. of Mg)	C ₄ Cl ₄ S (mole)	Iodine (g.)	THF (ml.)	Induction period ^b (hr.)	Reaction time (hr.)	Yield ^c by acid titra- tion ³⁷ (%)	Yield by carbon- ation (%)
10.2 (0.05)	0.05	0.6	120	2	13	96	84
18.9 (0.05)	0.05	0.6	120	2	14	89	79
30 (0.05)	0.05	0.6	120	1	14	82	71
39 (0.05)	0.05	0.6	120	$\frac{1}{2}$	8	89	76

^a The copper-magnesium alloys were obtained from the Dow Chemical Company, Midland Division, Michigan, to whom we wish to express our appreciation.

^b An approximate time taken for a positive response to Color Test I²². The reaction was conducted by stirring a mixture of tetrachlorothiophene, a copper-magnesium alloy and iodine (0.6g.) in THF.

^c Based on the starting amount of tetrachlorothiophene.

Table VII. Trichloro-2-thienylmagnesium halide from tetrachlorothiophene and magnesium in the presence of various catalysts

C ₄ Cl ₄ S (mole)	Mg (g.at.)	Catalyst (g.)	Solvent (ml.)	Reaction time (hr.)	Yield ^a %
0.05	0.055	-----	THF (100)	2 weeks	45 ^b
0.05	0.05	Iodine (0.5)	THF (50)	24	0
0.05	0.05	Iodine (0.5) + Cu/Mg (39%) (0.5)	THF (100)	40	13 ^c
				25	18 ^c
0.05	0.05	Cu/Mg (10.2%) activated ³¹ with iodine (0.5)	THF (100)	48	33 ^c
				78	98 ^{c,d}
0.05	0.05	C ₂ H ₄ Br ₂ (1-2 drops)	THF (30)	2	70 ^e

^a Based on the amount of tetrachlorothiophene.

^b Determined gravimetrically as 2,3,4-trichlorothiophene.

^c By acid titration³⁷.

^d Carbonation gave 2-C₄Cl₃SCo₂H in 62% yield.

^e By VPC (using durene as internal standard).

Table VIII. Reactions of trichloro-2-thienylmagnesium halide^a with metal halides and miscellaneous reagents

Reagents ^b (mole)	Reaction tempera- ture (°C)	Reaction period (hr.)	Products (% yield) ^c	Crystal- lizing solvent	m.p./ b.p. (°C)	Reported m.p./ b.p. (°C)
Me ₃ SiCl (0.05)	~27	2½	2-C ₄ Cl ₃ SSiMe ₃ (66,80) ^d	---	111- 116/ 15mm.	74/ 0.5 mm. ²⁵
HgCl ₂ (0.05)	~27	12	2-C ₄ Cl ₃ SHgCl (88)	Acetone- water	210- 211	211 ²⁶
CdCl ₂ (0.05)	~27	12	2-C ₄ Cl ₃ S·COCH ₃ ^e (10) ^f	---	---	---
H ₂ O	0	12	2-C ₄ Cl ₃ SH (66)	---	52-55/ 12.3mm.	209.2 -210.2 ²⁶
I ₂ /PhH (0.05)	0	12	2-C ₄ Cl ₃ SI ^g (65)	Methanol	49-50	50-51 ²⁶
CO ₂	0	6	2-C ₄ Cl ₃ SCOOH (87)	Chloro- form	226- 227	224 ²⁵
PhI (0.05)	65	12	no identi- fiable product	---	---	---

^a Prepared from tetrachlorothiophene (0.05 mole), magnesium (0.1 g. at.) and C₂H₄Br₂ (0.05 mole).

^b All reagents with the exception of iodine (which was added slowly as a benzene solution) were added in bulk and at one time.

^c Based on the amount of tetrachlorothiophene.

^d The yield was 66% when copper-magnesium alloy (30%) was used to prepare the Grignard reagent by the second method.

^e Subsequent to the addition of acetyl chloride and stirring at the ambient temperature for 12 hr. No ketone was formed when the reaction medium was benzene.

^f By VPC.

^g The Grignard reagent was added to the iodine solution.

Table IX. In situ preparation of various 2-silyltrichlorothiophenes

C ₄ Cl ₄ S (mole)	Metal or alloy (g.at. of Mg)	Reagent (mole)	Reaction tempera- ture (°C)	Time (hr.)	Major products (% yield)	Other products (% yield)
0.05	10.2% Cu-Mg (0.05)	Me ₃ SiCl (0.055)	~27	18	2-C ₄ Cl ₃ S·SiMe ₃ ^a <u>b</u> (67)	2,5-C ₄ Cl ₂ S (SiMe ₃) ₂ (<1)
0.05	18.9% Cu-Mg (0.05)	Me ₃ SiCl (0.055)	~27	24	2-C ₄ Cl ₃ S·SiMe ₃ ^a <u>b</u> (52)	---
0.05	30% Cu-Mg (0.05)	Me ₃ SiCl (0.055)	~27	10	2-C ₄ Cl ₃ S·SiMe ₃ ^a <u>b</u> (67)	2,5-C ₄ Cl ₂ S(SiMe ₃) ₂ (5)
0.05	39% Cu-Mg (0.05)	Me ₃ SiCl (0.055)	~27	24	2-C ₄ Cl ₃ S·SiMe ₃ ^a <u>b</u> (40)	2,5-C ₄ Cl ₂ S(SiMe ₃) ₂ (4)
0.05	30% Cu-Mg (0.05)	Ph ₃ SiCl (0.055)	~27	96	C ₄ Cl ₄ S { Ph ₃ Si ₂ { 38}; 30}	Ph ₃ SiOH (13)
0.05	30% Cu-Mg (0.05)	PhMe ₂ SiCl (0.05)	~27	28	2-C ₄ Cl ₃ S·SiPhMe ₂ ^a <u>b</u> <u>c</u> (48)	Ph ₂ Me ₄ Si ₂ ^c (23)
0.05	Mg (0.1)	Me ₃ SiCl (0.1)	56	48	2-C ₄ Cl ₃ S·SiMe ₃ ^a (50-55)	2,5-C ₄ Cl ₂ S(SiMe ₃) ₂ ^d (25-30) 2,3,5-C ₄ ClS(SiMe ₃) ₃ (1-2) ^e

^a Identified by comparing the IR spectra and VPC retention times with those of authentic samples. ^b C₄Cl₄S (4-6%) and 2-C₄Cl₃SH (3-6%) (and occasionally only a VPC-detectable amount of 2,5-C₄Cl₂H₂S) were formed. ^c Identified by VPC. ^d Identified by IR and mass spectra. ^e Not positively identified.

SECTION IV

TRICHLORO-2-THIENYLLITHIUM

1. INTRODUCTION AND DISCUSSION

In connection with the studies on the silylation of polyhalogenated compounds, carried out in these laboratories, we attempted to use the lithiation of tetrachlorothiophene for the preparation of some organosilicon and other derivatives of this heterocycle. It should be mentioned that the number of thienyl-silicon derivatives reported to date is rather small and no trichlorothienyl-silicon derivative is known. In order to compare the properties of organosilicon compounds containing pentachlorophenyl, tetrachloropyridyl and trichlorothienyl groups, it was necessary to synthesize some derivatives of the latter type.

The lithiation of tetrachlorothiophene through halogen-metal exchange with *n*-butyllithium, with the formation of trichloro-2-thienyllithium (I) was investigated by Bachman and Heisesy in 1948²⁸. The lithium reagent was carbonated to give trichloro-2-thiophenecarboxylic acid, and reacted with acetaldehyde and acetone to give the corresponding alcohols. More recently²⁹, several derivatives of transition metals, as well as a phosphorous and some mercury derivatives were reported.

2. EXPERIMENTAL

All reactions were carried out in a three-necked round-bottomed flask equipped with stirrer and dropping funnel under an atmosphere of dry, oxygen-free nitrogen. Glassware was dried at 120°C, assembled while hot, and flushed with dry nitrogen prior to introducing the reagents. Commercial solutions of alkyl- and aryllithium reagents (Foote Mineral Co.), tetrachlorothiophene (Aldrich Chemical Co. and Hooker Chemical Co.) and organochlorosilanes (Union Carbide Corp.) were used as received. Ph_3SiCl from Arapahoe Chemicals, and Ph_2PCl from Aldrich were used without further purification. Etheral solvents and THF were distilled from sodium-benzophenone ketyl. All other solvents were used without further purification. VPC analyses were determined on an F & M Model 500 Gas Chromatograph using a 4 ft. column of Silicone Gum Rubber (15% on Chromosorb W).

a. Preparation of trichloro-2-thienyllithium (I)

Trichloro-2-thienyllithium was prepared by a variety of methods of which the following two are representative. Method A is the preferred method.

(1) Method A

To a 250 ml. three-necked flask was added 11.06 g. (0.05 mole) of tetrachlorothiophene and 100 ml. of dry ether. The mixture was cooled with stirring to -15°C to -17°C and 0.05 mole of *n*-BuLi (1.6 N in hexane) was added during ca. 15 min. The mixture was stirred until Color Test II²² was negative (indicating the disappearance of *n*-BuLi; 35-45 min.). The resulting solution was a pale-straw color which darkened with time or on warming. The solution gave a strong positive Color Test I²². No evidence of a precipitate was observed and hydrolyzed aliquots, examined by VPC, showed that the area of a single peak (due to 2,3,4- $\text{C}_4\text{Cl}_3\text{HS}$) comprised greater than 99.5% of the total area (other than solvent), much of the remainder being due to unreacted tetrachlorothiophene.

(2) Method B

This method was similar to Method A except that the temperature of the reaction was kept at -70°C . The time required to give a negative Color Test II²² was 10-12 hr. Examination of hydrolyzed aliquots by VPC showed that 2,3,4- $\text{C}_4\text{Cl}_3\text{HS}$ was again the major product (> 98%). An increase in the amount of unreacted $\text{C}_4\text{Cl}_4\text{S}$ (~ 1-2%) over that observed in Method A was noted. Again the solution was a very pale-straw color.

b. Carbonation

Each of the following organolithium solutions was carbonated by cooling to -70°C and adding a large excess of crushed Dry Ice. The cooling bath was then removed and the slurry stirred until it attained room temperature. The mixture was hydrolyzed (3N, HCl, 100 ml.) and the ether layer separated. The acid in the ether layer was extracted into aqueous Na_2CO_3 solution. This was then acidified and the organic acid extracted into ether (~ 200 ml.) which was evaporated to leave the solid acid. Recrystallization from CHCl_3 gave trichloro-2-thiophenecarboxylic acid, m.p. $226-7^{\circ}$ [cited²⁸: 224°].

Using Method A for the preparation of (I), the yield of acid (based on tetrachlorothiophene) was 99% in a 0.05 mole run. With Method B, the yield was 93%.

In another experiment, tetrachlorothiophene (0.05 mole) dissolved in 150 ml. of THF, was cooled to -70°C and an equimolar quantity of *t*-BuLi in pentane was added dropwise during 15-20 min. The reaction mixture was then stirred at -70°C until Color Test II was negative (2.5-3.5 hr.). The yield of acid was 91%.

c. Reaction with chlorotrimethylsilane

To trichloro-2-thienyllithium (Method A, 0.05 mole) was added chlorotrimethylsilane (0.055 mole, 10% excess) and the mixture stirred from -17°C to room temperature for 8 hr. The mixture was then hydrolyzed at 0°C with 3N HCl and the ether layer separated, dried over MgSO_4 and evaporated to give 13.4 g. of an oil. Distillation afforded trichloro-2-thienyltrimethylsilane (11.8 g.; 91%) b.p. 74°C/0.5 mm. The IR, and NMR spectra as well as the VPC retention time were identical with an authentic sample³⁵. This reaction was repeated on several occasions with yields ranging from 89 to 91%.

d. Reaction with chlorophenyldimethylsilane

To trichloro-2-thienyllithium (0.05 mole, Method A) at -15°C was added (0.055 mole, 10% excess) of chlorophenyldimethylsilane, and the mixture allowed to come to room temperature. After stirring 7 hr. the mixture was worked up as in (c) to yield 16.0 g. of an oil. Distillation on a spinning band column gave trichloro-2-thienylphenyldimethylsilane (14.3 g., 89%) b.p. 127°C/0.15 mm. [Found: Cl, 32.89%. Calc. for $\text{C}_{12}\text{H}_{11}\text{Cl}_3\text{SSi}$: Cl, 33.06%.] [Molecular weight*: found 322; calc. 321.7.]

e. Reaction with chlorotriphenylsilane

To trichloro-2-thienyllithium (0.15 mole) at -15°C was added chlorotriphenylsilane, 44.3 g. (0.15 mole) and the mixture allowed to come to room temperature. After 15 hr., the reaction was hydrolyzed with 3N HCl, the ether layer separated and evaporated to give 80 g. of a solid, m.p. 100-127°C. This solid was extracted into petroleum ether (b.p. 60-70°C), which on concentration and recrystallization gave 47 g. of solid, m/p. 106-122°C. This was dissolved in the minimum volume of petroleum ether and chromatographed on a silica gel column using petroleum ether as the eluent. The eluent yielded 29 g. of a solid, m.p. 109-111°C. Treatment with activated charcoal and recrystallization from methanol gave 26.5 g. (39%) of trichloro-2-thienyltriphenylsilane m.p. 110.5-111°C. [Found: C, 59.5%; H, 3.45%; Si, 6.27%. Calc. for $\text{C}_{22}\text{H}_{15}\text{Cl}_3\text{SSi}$: C, 59.27%; H, 3.39%; Si, 6.30%.] The molecular weight was determined by mass spectrometry. [Found: 447; Calc. 445.9.]

*Molecular weights were determined by mass spectrometry. Values given are the center of the cluster of peaks due to the molecular ion. The isotopic pattern and intensities were what one would expect from compounds containing three chlorine atoms.

f. Reaction with dichlorodimethylsilane

To trichloro-2-thienyllithium (0.05 mole) at -15°C was added 3.2 g. (0.025 mole) of dichlorodimethylsilane and the mixture allowed to come to room temperature. The mixture was stirred for 4 hr., hydrolyzed with 3N HCl and the ether layer separated. Evaporation of the solvent gave 11.4 g. of an oil which solidified on standing. Recrystallization from petroleum ether gave 8.3 g. (76%) of bis(trichloro-2-thienyl)dimethylsilane, m.p. $89-90^{\circ}\text{C}$. Sublimation gave an analytical sample, m.p. $90-90.5^{\circ}\text{C}$. [Found: Cl, 49.57%. Calc. for $\text{C}_{10}\text{H}_6\text{Cl}_2\text{S}_2\text{Si}$: Cl, 49.34%.] The molecular weight was determined by mass spectrometry. [Found: a complex pattern centered at 432; Calc. 431.1.]

g. Reaction with chlorodimethylhydrosilane

To trichloro-2-thienyllithium (0.05 mole, Method A) at -10°C was added 4.75 g. (0.05 mole) of chlorodimethylhydrosilane and the mixture stirred overnight, during which time the reaction warmed to room temperature. Work-up (as in (f)) gave 11.8 g. of an oil. Distillation on a spinning band column gave 10.8 g. (88%) of trichloro-2-thienyldimethylhydrosilane, b.p. $81-82^{\circ}\text{C}/1.0$ mm. [Found: Cl, 43.13%. Calc. for $\text{C}_6\text{H}_7\text{Cl}_3\text{SSi}$: Cl, 43.31%.] The molecular weight was determined by mass spectrometry. [Found: 246; Calc. 245.6.] A similar reaction (0.2 mole scale) gave an 84% yield of the trichloro-2-thienyldimethylhydrosilane.

h. Reaction with chlorodiphenylphosphine

To trichloro-2-thienyllithium (0.05 mole) prepared³⁵ in THF at -70°C was added 11.0 g. (0.05 mole) chlorodiphenylphosphine. The mixture was stirred for 15 hr. during which time the reaction rose to room temperature. The mixture was filtered, evaporated, extracted into benzene, and the benzene evaporated to give 11.5 g. of a solid, m.p. $95-103^{\circ}\text{C}$. This was treated with activated charcoal in hot petroleum ether, filtered, concentrated, and cooled to deposit white crystals (9.1 g. 49%) of trichloro-2-thienyldiphenylphosphine, m.p. $113-115^{\circ}\text{C}$. Sublimation of a 2.0 g. portion gave virtually a quantitative yield of white solid, m.p. $116.5-117^{\circ}\text{C}$ (Cited²⁹: $115-116^{\circ}\text{C}$).

SECTION V

3,4-DICHLORO-2,5-DILITHIOTHIOPHENE

1. INTRODUCTION AND DISCUSSION

In the preceding Sections we have shown how readily accessible are the mono-Grignard and the mono-organolithium compounds situated in an alpha-position of trichlorothiophene. It is possible to prepare 3,4-dichloro-2,5-di(MgX)thiophene. However, at this stage it is not a convenient procedure. Fortunately, we have developed a highly satisfactory route to 3,4-dichloro-2,5-dilithiothiophene. This relatively reactive di-organometallic compound has a special attractiveness for our general program because it permits the ready formation of essentially all types of 3,4-dichloro-2,5-di(organometallic)thiophenes in accordance with the generalizations we made some years ago. With such types, there are available methods for the introduction of an unusually diversified series of di-functional derivatives or monomers which should lend themselves to the preparation of useful polymers. For example, the two C-Li units in the alpha-positions of the dichlorothiophene can be readily converted to the corresponding di-organocopper compounds.

2. EXPERIMENTAL

All reactions were performed in an atmosphere of dry nitrogen in a three-necked flask equipped with a stirrer and a dropping funnel. Glassware was dried at 120°C, assembled while hot and flushed with dry nitrogen prior to introducing the reagents. Commercial solutions of *n*-butyllithium in hexane (Foote Mineral Co.) and organochlorosilanes (Union Carbide Corp. and Dow-Corning Corp.) were used as supplied. Ether and THF were distilled from sodium-benzophenone ketyl. All other solvents were used without further purification. VPC analyses were effected on an F and M Model 500 Gas Chromatograph using 4 ft. columns of Silicon Gum Rubber (15% on Chromosorb W) and D.C. Silicone Oil 710 (20% on Chromosorb W).

a. Preparation of 2,5-dilithiodichlorothiophene.

To a 500 ml. reaction flask was added 11.06 g. (0.05 mole) of tetrachlorothiophene and 100 ml. of dry ether. The mixture was cooled to 15°C and *n*-BuLi (0.105 mole, 5% excess) was added during 10-15 min. The reaction mixture was stirred for one hr. and derivatized. The solution gave a strongly positive Color Test I²². Some spectral data for the various derivatives are given in Table X.

(1) Dichlorothiophene-2,5-dicarboxylic acid.

A large excess of solid CO_2 was added to 2,5-dilithiodichlorothiophene. The reaction mixture was stirred for ca. 4 hr. as it came to room temperature. The mixture was then hydrolyzed with dil. HCl (200 ml. of 3N) and the ether layer separated. The acid was extracted into aqueous Na_2CO_3 which was then acidified and the acid redissolved in fresh ether. Evaporation of the ether layer yielded a white crystalline material (5.4 g., 90%) m.p. 322-327°C. Two recrystallizations from acetone-water mixture gave 5.2 g. (87%) m.p. 330-1°C. [Cited³⁸: 314-315°C] The material was titrated in $\text{EtOH}/20\% \text{H}_2\text{O}$ with aqueous NaOH . [Found: equivalent wt., 121.3, 121.6. Calc. for $\text{C}_6\text{Cl}_2\text{H}_2\text{O}_4\text{S}$: 120.5]

(2) 2,5-bis(Trimethylsilyl)dichlorothiophene.

To 0.05 mole of 2,5-dilithiodichlorothiophene was added 12.4 g. (0.11 mole, 10% excess) of chlorotrimethylsilane. The mixture was stirred at room temperature for 48 hr., filtered, and the solvent evaporated to yield 14.7 g. of a brown oil. VPC showed that the oil consisted of some solvent, trichloro-2-thienyltrimethylsilane (much less than 1%) and a product of longer retention time. Distillation afforded 11.9 g. (80%) of a liquid, b.p. 79°C/0.07 mm. VPC showed this to be > 99.9% pure. [Found: C, 40.0; H, 6.24; Si, 19.1%. Calc. for $\text{C}_{10}\text{Cl}_2\text{H}_{18}\text{Si}_2$: C, 40.39; H, 6.10; Si, 18.89%.]

(3) 2,5-bis(Dimethylhydrosilyl)dichlorothiophene.

To 2,5-dilithiodichlorothiophene (0.05 mole) prepared in the usual way was added 10.0 g. (0.105 mole, 5% excess) of chlorodimethylhydrosilane in 20 ml. of dry ether during 10 min. When approximately three-fourths of the silane had been added, a bright violet color appeared which lasted for about 3 min., then disappeared to leave a white precipitate. The reaction was stirred for 8 hr. and worked up as in (2) to give 14.0 g. of an oil. Distillation afforded 10.1 g. (82%) of 2,5-bis(dimethylhydrosilyl)dichlorothiophene, b.p. 92°C/1.0 mm. [Found: C, 35.5; H, 5.38; Si, 21.6%. Calc. for $\text{C}_8\text{Cl}_2\text{H}_{14}\text{Si}_2$: C, 35.68; H, 5.24; Si 20.86%.]

(4) Reaction of 2,5-dilithiodichlorothiophene and dimethyldichlorosilane.

The dilithium compound (0.05 mole) was prepared as described and treated with 6.4 g. (0.05 mole) of Me_2SiCl_2 . After 6 hr. the mixture was hydrolyzed and worked up to give an ether-insoluble material. The white solid softened at 230°C, became transparent at about 240°C and began to flow at ca. 250°C. The yield is 5.4 g. (51% based on $(-\text{C}_4\text{Cl}_2\text{S SiMe}_2)_n$). The material is insoluble in the usual solvents; (ether, ethanol, chloroform, acetone and hexane).

(5) Reaction of 2,5-dilithiodichlorothiophene and diphenylhydrochlorosilane.

To the dilithium derivative (0.05 mole, prepared as described above) was added 12.0 g. (0.11 mole, 10% excess) of Ph_2HSiCl and the reaction mixture stirred for 10 hr. An anhydrous work-up (as in(2)) of the reaction mixture yielded a very viscous brown oil. An attempt to distill this oil by ordinary means was not successful. After 5 months, no crystals had formed in the oil.

(6) Reaction of 2,5-dilithiodichlorothiophene and tetrachlorothiophene.

To the dilithium compound (0.05 mole) was added 5.5 g (0.025 mole) of tetrachlorothiophene. The mixture was stirred at room temperature for 78 hr. during which time the reaction was monitored by VPC (4 ft. column, D.C. Silicone Oil 710, 150°C). The reaction was slow but after 78 hr. the mixture (subsequent to hydrolysis) consisted of 8% tetrachlorothiophene, 49% 2,3,4-trichlorothiophene and 43% 3,4-dichlorothiophene. After 78 hr. the mixture was carbonated to give 10.6 g. of a mixture of trichlorothiophene-2-carboxylic acid and dichlorothiophene-2,5-dicarboxylic acid. No separation of these two acids could be achieved by recrystallization.

Table X. Spectral Data For Some Derivatives of 2,5-Dilithiodichlorothiophene



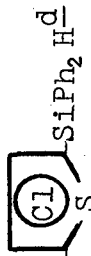
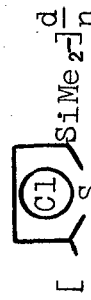
Compound	IR (cm ⁻¹) ^a	NMR (τ) ^b	Mass Spec. (m/e) ^c
 Me ₃ Si-(C ₆ H ₄) ₂ -SiMe ₃	2950 (m), 2890 (sh) C-H; 1502 (m), 1410 (s), 1308 (s), 1278 (w), -(3,4-C ₄ Cl ₂ S)-; 1250 (s), 842 (vs) -SiMe ₃ .	Singlet at 9.62	(M ⁺) 296, 298, 300 (Calc. 297.4); (M-CH ₃) ⁺ 281, 283, 285 (Calc. 282.4).
 HMe ₂ Si-(C ₆ H ₄) ₂ -SiMe ₂ H	2970 (m), 2900 (sh) C-H; 2140 (s) Si-H; 1470 (w), 1395 (m), 1300 (s), 1280 (s) -(3,4-C ₄ Cl ₂ S)-; 1250 (s), 840 (vs), 768 (s) -SiMe ₂ .	Multiplet 5.48 due to Si-H; Doublet at 9.58 (J=3.7 CPS) due to methyl protons Integration 0.96:6.0 (Calc. 1:6).	(M ⁺) 268, 270, 272 (Calc. 269.3); (M-CH ₃) ⁺ 253, 255, 257 (Calc. 254.3).
 HPh ₂ Si-(C ₆ H ₄) ₂ -SiPh ₂ H ^d	3030-2900 (m, broad) C-H; 2140 (s) Si-H; 1480 (w), 1302 (m), 1280 (s), -(3,4-C ₄ Cl ₂ S)-; 1425 (s), 1110 (s) Si-Ph.		
 [SiMe ₂ (C ₆ H ₄) ₂] _n ^d	2910 (m, broad) C-H; 1460 (w), 1385 (m), 1320 (m), 1280 (s) -(3,4-C ₄ Cl ₂ S)-; 1250 (s), 840 (s), 808 (s, broad)-SiMe ₂ - ^e .		

Table X Continued

Footnotes:

- a Taken on NaCl plates as neat liquids: m = medium, s = strong, sh = shoulder, vs = very strong, w = weak
- b Determined as solutions in CCl_4 ; values are relative to TMS.
- c In each case the isotopic pattern and intensities were as expected for a compound containing two chlorine atoms.
- d Not positively identified.
- e The spectrum was taken from a KBr disk.

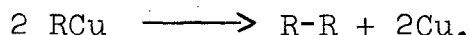
SECTION VI

TRICHLORO-2-THIENYLCOPPER

1. INTRODUCTION AND DISCUSSION

Trichloro-2-thienylcopper can be prepared by reaction of trichloro-2-thienyllithium or trichloro-2-thienylmagnesium chloride with CuX ($\text{X} = \text{Cl}, \text{I}$) in solvents such as THF and diglyme, or with CuI in ether. With either the lithium or Grignard reagents, satisfactory yields are obtained.

The solvent used appears to play an important part in the preparation of the copper compound. When a good donor solvent such as THF or diglyme was used, the reaction proceeded smoothly even at low temperatures. In diethyl ether, on the other hand, the reaction with CuCl was not complete at -70°C even after extended time (72 hr.). The reaction seemed to require higher temperature (ca. -35°C) to proceed at all and then gave hexachloro-2,2'-bithienyl as the principal product, regardless of the derivatizing reagent added. (Previous work²³ had shown that ether was less suitable for the preparation of $\text{C}_6\text{F}_5\text{Cu}$ by a similar reaction.) It was thought that this biaryl could arise through decomposition of the copper compound at these higher temperatures in ether. When trichloro-2-thienylcopper was prepared from the more reactive CuI in ether at -70°C , no hexachloro-2,2'-bithienyl could be isolated. However, when the copper compound prepared in this manner was allowed to warm to room temperature, no decomposition was apparent. Accordingly, unless there are appreciable differences in the copper compound (or its complex) prepared by the two methods, thermal decomposition of an intermediate copper compound may not be a likely explanation of the high yields of the coupling product. It has been shown* that $\text{C}_6\text{F}_5\text{Cu}$ as well as aryl- and alkylcopper compounds can decompose, at least in part, to give biaryls or bialkyls:



The conventional route of decomposition, through an "aryne" intermediate is unlikely to occur with the trichlorothiophene derivatives.** In solvents such as THF and diglyme, only small amounts of hexachloro-2,2'-bithienyl were isolated.

The method of preparation as regards the use of CuI or CuCl seems to make a large difference only in ether, although the yields in other solvents were somewhat improved when CuI was used. This probably reflects a facile preparation rather than a difference in reactivity of the copper compound prepared in this way. The readily available and inexpensive CuCl was used in most reactions because it was felt that the small increase in yield did not justify the use of CuI .

*A. E. Jukes, S. S. Dua and H. Gilman, J. Organometal. Chem., **24**, 791 (1970). **G. Wittig, personal communication; see also G. Wittig and M. Rings, Justus Liebigs Ann., **719**, 127 (1968).

2. EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen in glassware dried at 110°C and assembled while hot. Ethereal solvents were distilled from sodium-benzophenone ketyl. *t*-Butyllithium in pentane and *n*-butyllithium in hexane were from Foote Mineral Co. Copper(I) chloride was a commercial sample which was further purified prior to use. VPC analyses were made on an F and M Model 500 Gas Chromatograph with a 4' x 1/4" column packed with 15% Silicon Gum Rubber on Chromosorb W (60-80 mesh).

a. Preparation of trichloro-2-thienylcopper(I)

(1) Method I: In THF

To trichloro-2-thienyllithium, prepared in 100 ml. THF at -70°C from 11.06 g. (0.05 mole) of tetrachlorothiophene and 0.05 mole *t*-butyllithium, was added 0.05 mole of CuX (X = Cl, I). The reaction mixture was stirred at -70°C until Color Test I²² was negative (5-6 hr., X = Cl; 2 hr., X = I). An equivalent of the appropriate derivatizing reagent in ca. 30 ml. THF was added dropwise (2 drops/sec.), the cooling bath removed, and the reaction mixture stirred the desired length of time (until VPC indicated that the copper compound had been consumed). In an alternate procedure, trichloro-2-thienylmagnesium halide (prepared by an entrainment method, see SECTION III) was treated with CuCl. After 2 hr., Color Test I²² was negative. The reaction mixture was stirred an additional 4 hr. and derivatized as above. The work-up consisted of hydrolysis of the reaction mixture with NH₄Cl solution. Petroleum ether (100 ml.) was added and the organic layer was separated and washed with three 100 ml. portions of a solution of 50% of a saturated solution of NH₄Cl in water and 50% conc. NH₄OH followed by three washings (100 ml. each) with water. The organic layer was dried (MgSO₄) and the solvent evaporated. The derivative was then purified by an appropriate procedure (see Tables XI and XII).

(2) Method II: In ether/THF (1/1)

Trichloro-2-thienyllithium, prepared in 100 ml. ether at -15°C from tetrachlorothiophene (0.05 mole) and *n*-butyllithium (0.05 mole) was cooled to -70°C and THF (100 ml.) was added slowly. Copper(I) chloride (4.95 g., 0.05 mole) was added and the mixture stirred until Color Test I²² was negative (8-10 hr.)**. The copper compound (I) was derivatized and worked up in the same way as in Method I.

**It was subsequently discovered that the preparation of the copper compound(I) could be expedited by allowing the reaction mixture to warm slowly (4 hr.) to 0°C immediately after the CuCl was added.

(3) Method III: In monoglyme

To trichloro-2-thienyllithium, prepared in 100 ml. monoglyme at -70°C from 11.06 g. (0.05 mole) tetrachlorothiophene and 0.05 mole *n*-butyllithium, was added 0.05 mole CuX ($\text{X} = \text{Cl}, \text{I}$). The reaction mixture was stirred until Color Test I was negative (8 hr., $\text{X} = \text{Cl}$; 4-5 hr., $\text{X} = \text{I}$). Derivatization and work-up were previously described (Methods I and II).

(4) Method IV: In ether

Copper(I) chloride (0.05 mole) was added to trichloro-2-thienyllithium (0.05 mole) in 100 ml. ether at -70°C . After 11 hr., the reaction was not complete (positive Color Test I). The reaction was warmed until at -23°C there was a change in color from pale yellow to green. After 4 hr. at ca. -25°C , Color Test I was negative. Considerable precipitate formed. Addition of acetyl chloride and the usual work-up gave 6.7 g. (72%) of hexachloro-2,2'-bithienyl, m.p. $190-190.5^{\circ}\text{C}$ [cited³⁸: $189.5-190^{\circ}\text{C}$], identical with an authentic sample prepared from the reaction of trichloro-2-thienyllithium and CuCl_2 in ether. No acetyl derivative was isolated.

A similar reaction at -15°C for 3.5 hr. gave on hydrolysis and work-up, 6.8 g. (73%) of hexachloro-2,2'-bithienyl.

From a third reaction several 5 ml. aliquots were withdrawn which showed that no derivatizing agent (i.e. acetyl chloride or H_2O) was necessary for coupling to give the biaryl. From the reaction was isolated 6.3 g. (67%) of hexachloro-2,2'-bithienyl.

When trichloro-2-thienyllithium was reacted with CuI in ether at -70°C , Color Test I was negative after 9 hr. Derivatization and work-up were as above.

(5) Method V: From lithium dimethylcuprate

To lithium dimethylcuprate⁴ (0.10 mole) in 100 ml. THF at -15°C was added 0.10 mole of tetrachlorothiophene. The mixture was stirred for 18 hr. VPC showed only ca. 10% of the copper compound(I) had been formed. Derivatization and work-up were as above (Method I).

(6) Method VI: By an in situ-entrainment method

To 0.05 mole tetrachlorothiophene, 0.11 g.-atom (10% excess) Mg and 0.06 mole (20% excess) CuCl in 100 ml. THF was added slowly (3 hr.) 9.4 g. (0.05 mole) of ethylene bromide, and the mixture stirred for 16 hr. VPC showed only ca. 55% of (I) was formed. The compound was derivatized and worked up as previously described (Method I).

The results of the different methods of preparation of (I) are presented in Table XI. The yields and properties of selected derivatives prepared from the copper compound (I) are in Table XII.

Table XI. Yields of 2-Acetyltrichlorothiophene by various methods

Method ^a	Solvent	CuX	Time ^b (hr.)	Yield of C ₄ Cl ₃ S-2-COMe ^{c,d}	Yield of C ₄ Cl ₃ S-2-C ₂ H ₅ ^e
I	THF	CuCl	16	7.2 g; 63%	-----
I	THF	CuI	5	8.7 g; 76%	-----
II	THF/Et ₂ O	CuCl	4	8.2 g; 71%	0.37 g; 3%
III	Monoglyme	CuCl	5	7.9 g; 69%	0.12 g; 1%
III	Monoglyme	CuI	5	8.5 g; 74%	0.06 g; 0.5%
IV	Et ₂ O	CuCl	3.5-110	-----	57-73%
V	THF	-----	18	f 6%	-----
VI	THF	CuCl	16	3.8 g; 33%	-----
I ^h	THF	CuCl	4 ⁱ	6.9 g; 60% ^j	-----

^a See the experimental section for details. ^b After the addition of 10% excess acetyl chloride. ^c Based on 0.05 mole of tetrachlorothiophene used to prepare the copper compound. ^d The compound was recrystallized from petroleum ether (60-70°) and sublimed, m.p. 78.5-79°C, cited³ 80°. ^e The compound was recrystallized from xylenes, m.p. 189-190°C, cited³ 189.5-190°C. ^f Yield determined by VPC. ^g Difficulty was experienced in purification. ^h Prepared from 2-C₄Cl₃SMgX. ⁱ After the addition of acetyl chloride in 100% excess. ^j Purity was 95% by VPC.

Table XII. Derivatives From Trichloro-2-thienylcopper

Method ^a	Derivatizing Reagent	Temp. (°C)	Time ^b (hr.)	Derivative ^c	Recrystallization solvent	m.p. or b.p. °C/mmHg	Yield ^d	Analysis % Cl: Found (Calc.)
I	BzCl	25	72	R-Bz	Pet. ether ^e ; sublimed	69-70	7.2 g.; 58%	f (36.47)
I	PhI	110 ^g	38	R-Ph	Pet. ether ^e ; sublimed	63.5-4	5.9 g.; 53%	40.53 (40.35)
II ^h	trans-(ClC(O)CH:) ₂	25	18	trans-(RC(O)CH:) ₂	acetone/hexane; CHCl ₃	203-4	6.4 g.; 55%	46.53 (46.75)
II ^h	CH ₂ :CHCH ₂ Br	25	6	R-CH-CH=CH ₂	---	64/0.5	7.1 g.; 62%	46.90 (46.74)

^a See experimental section for details. Solvent was THF. ^b After the addition of the derivatizing reagent. ^c R=2-C₄Cl₃S-. ^d Based on 0.05 mole tetrachlorothiophene. ^e Petroleum ether (60-70°C). ^f I.R. shows C = O at 1630 cm⁻¹; NMR shows phenyl protons centered at 2.35τ. ^g No reaction was observed after refluxing for 6 hr. in THF (ca. 60°C). The solvent was replaced by 2,2',4,4'-tetramethyltetrahydrofuran (121°C) and heated. ^h a mixture of ether and THF was the solvent.

SECTION VII

3,4-DICHLORO-2,5-DICOPPERTHIOPHENE

1. INTRODUCTION AND DISCUSSION

The usefulness of dimetallic derivatives such as 3,4-dichloro-2,5-dicopperthiophene was mentioned in a preceding section (V). There are several standard procedures now available for preparing perhalo-organocopper compounds. We have found the reaction between 3,4-dichloro-2,5-dilithiothiophene with cuprous halides to be satisfactory, and this is described in the following Experimental Part.

2. EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen in a 500 ml. three-necked flask equipped with a stirrer, a dropping funnel and a nitrogen inlet. Commercial *n*-butyllithium in hexane (Foote Mineral Co.) was used. CuCl was a commercial sample purified by a reported procedure²¹. CuI was from Alpha Inorganics. Ether and THF were distilled from sodium-benzophenone ketyl prior to use. All other solvents were used without further purification. Tetrachlorothiophene was from Hooker Chemical Corp.

a. Preparation of 2,5-bis(copper(I))dichlorothiophene

The 2,5-dilithiodichlorothiophene was prepared in ether in the usual way (Section V) and then cooled to -70°C (Dry Ice-acetone). To this was slowly added THF (150-200 ml.) followed immediately by the copper(I) halide (CuCl or CuI). The mixture was then stirred and allowed to warm slowly to ca. 0°C . The progress of the reaction was monitored by checking Color Test I. It appeared that little or no reaction occurred between CuX (X = Cl, I) and the lithium compound until the temperature reached about -20°C . When the formation of the copper compound was complete, the reaction mixture consisted of a brown paste suspended in a light brown solution. The compound was derivatized as described below.

(1) Preparation of 2,5-bis(acetyl)dichlorothiophene

To 2,5-bis(copper(I))dichlorothiophene (0.05 mole) prepared as described above via CuCl was added acetyl chloride (8.7 g., 0.11 mole, 10% excess in 20 ml. ether) and the mixture stirred for 21 hr. The mixture was hydrolyzed and worked up in the manner customarily used for copper compounds (see previous Section VI, Method I). An oil and a solid (intermixed) were obtained. These were dissolved in the minimum amount of petroleum ether ($60-70^{\circ}\text{C}$)

and chromatographed on a silica gel column to yield 7.5 g. of a solid m.p. 171-173°C. After recrystallizing from xylene and 2:1 acetone-petroleum ether mixture, there was recovered 7.2 g. (61%) of 2,5-bis(acetyl)dichlorothiophene, m.p. 172.5-173.5°C. [Found: Cl, 29.97%. Calc. for $C_8Cl_2H_6O_2S$: Cl, 29.90%.] The mass spectrum shows $(M)^+$ at 236, 238, 240 (Calc. 237.1); $(M-CH_3)^+$ at 221, 223, 225 (Calc. 222.1) mass units. Similar preparations using CuI instead of CuCl gave the bis-acetyl derivative in 60-64% yield. A reaction in which acetyl chloride was added to the dilithio derivative gave only a tarry material. No bis-acetyl derivative could be detected by VPC.

(2) 2,5-Diiododichlorothiophene

To 2,5-bis(copper(I))dichlorothiophene (0.05 mole) prepared via CuCl was added 27.9 g. (0.11 mole) of solid iodine. The reaction mixture was stirred at -30°C for 12 hr., allowed to come to room temperature and stirred for an additional 12 hr. Work-up as above gave a dark brown solid (17.8 g.) m.p. 96-98°C. The material was chromatographed on a silica gel column using hexane as the eluent. A light yellow material (13.2 g.), m.p. 99-101°C was recovered. The material was sublimed to give 11 g. of a solid m.p. 99-102°C. The residue was a yellow powder (0.8 g.), m.p. 197-199°C which may be tetraiodothiophene [cited³⁸: 199°C]. The bulk of the material was recrystallized from Skelly B then from 100% ethanol to yield 10.5 g. (52%) of 2,5-diiododichlorothiophene, m.p. 102-102.5°C [cited³⁸: 106°C]. Repeated recrystallizations did not change the melting point. The mass spectrum of the compound shows $(M)^+$ at 404, 406, 408 (Calc. 404.9); $(M-I)^+$ at 277, 279, 281 (Calc. 277.9); $(M-2I)^+$ at 150, 152, 154 (Calc. 150.9) mass units.

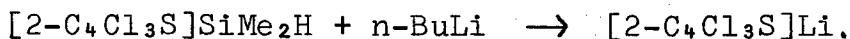
SECTION VIII

CONVERSION OF C-SiMe₂H TO C-Li

1. INTRODUCTION AND DISCUSSION

This particular conversion or replacement reaction was developed incidental to an examination of the C-SiMe₂H systems in polychlorothiophenes. It may prove to be a very useful reaction for several studies one of which concerns the formation of the very important HMe₂Si-(CF₂)_n-SiMe₂H and M-(CF₂)_n-M types.

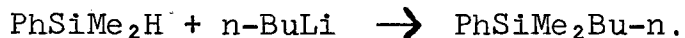
When trichloro-2-thienyldimethylsilane, [2-C₄Cl₃S]SiMe₂H is treated with n-BuLi under very moderate conditions the following smooth reaction occurs:



The trichloro-2-thienyllithium so formed gives, on carbonation, a 90% yield of trichloro-2-thiophenecarboxylic acid. Under corresponding conditions the [2,5-C₄Cl₂S](SiMe₂H)₂ gives an 87% yield of [2,5-C₄Cl₂S](CO₂H)₂. With C₆F₅SiMe₂H the yield of C₆F₅CO₂H is 80%; and from [4-C₅Cl₄N]SiMe₂H the yield of tetrachloro-4-pyridinecarboxylic acid, [4-C₅Cl₄N]CO₂H is 86%. These two reactions are of particular and somewhat related significance. First, there is the promise of using the reaction with the HMe₂Si-(CF₂)_n-SiMe₂H and also, of course, with the CF₃(CF₂)_n-SiMe₂H types. Secondly, the [4-C₅Cl₄N]Li that is formed is unusually clean and neat, unlike other preparations of this tetrachloro-4-pyridyllithium; and the facile conversion of C-SiMe₂H to C-Li may promise a long-desired route to important monomers having three halogens and two C-M units attached to the pyridine nucleus.

It should be stated that the reaction with C₆Cl₅SiMe₂H is not so high-yielding due to some secondary reactions not too rigorously defined at this time.

There is a marked contrast with the reaction of phenyldimethylsilane with n-BuLi under corresponding conditions wherein the -SiMe₂H is smoothly converted in 86% yield to -SiMe₂Bu-n:



This type of reaction does not occur under corresponding conditions with [2-C₄Cl₃S]SiMe₃; and there is formed, after carbonation, a 91% yield of 3,4-dichloro-5-trimethylsilyl-2-thiophenecarboxylic acid.

There is essentially no reaction, under corresponding conditions, with the following combinations: (a) [2-C₄Cl₃S]SiMe₂H or (b) [2,5-C₄Cl₂S](SiMe₂H)₂ with n-BuMgBr; (c) PhSiMe₂Bu-n with n-BuLi; and (d) [2-C₄Cl₃S]SiMe₃ with n-BuMgBr.

2. EXPERIMENTAL

All reactions were effected under an atmosphere of dry nitrogen in a three-necked round-bottom flask equipped with a nitrogen inlet tube, dropping funnel and sealed stirrer. The equipment was dried at 120°C, assembled while hot and flushed with dry nitrogen prior to charging the flask with the reactants. *n*-Butyllithium (1.6N in hexane) and methyllithium (1.7N in ether/benzene) were from the Foote Mineral Co. Ether was distilled from sodium benzophenone ketyl. All other solvents were used without further purification. Pentachlorophenyl-³⁹, tetrachloro-4-pyridyl-², pentafluorophenyl-⁴⁰, phenyl-⁴¹ and trichloro-2-thienyldimethylsilanes, 2,5-bis(dimethylsilyl) dichlorothiophene, 2,5-bis(trimethylsilyl)dichlorothiophene, and trichloro-2-thienyltrimethylsilane (see this report, sections IV and V) were prepared by the reported procedures.

a. General Procedure

The reaction flask was charged with ca. 80 ml. of dry ether and the appropriate silane and cooled to -70°C with a Dry Ice-acetone bath. To this solution, with vigorous stirring was added dropwise an equivalent quantity of the alkyllithium. The reactions were monitored by inspection of VPC curves of small aliquots after either hydrolysis and/or treatment with Me₃SiCl. When the particular reaction seemed to be complete, it was derivatized. The details of the various reactions are contained in Table XIII. The reactions which were carbonated were worked-up as described in Section IV for trichloro-2-thiophenecarboxylic acid. The silane derivatives were worked-up as described in Section IV for trichloro-2-thienyldimethylhydrosilane. Liquids were distilled and solids were recrystallized from petroleum ether.

Table XIII. Reaction of Aryl and Polyhaloaryl Dimethyl- and Trimethylsilanes with Alkyl-metallic Reagents in Ether

Silane (Mole)	RM (Mole)	Temp. (°C) (Maximum)	Time	Derivatizing Reagent	Products ^a	Yield ^b
2-C ₄ Cl ₃ SSiMe ₂ H (0.025)	n-BuLi (0.025)	-70	10 min.	CO ₂	2-C ₄ Cl ₃ SCOOH	5.2 g. 90%
2-C ₄ Cl ₃ SSiMe ₂ H (0.02)	n-BuMgBr (0.02)	60°	48 hr.	---	2-C ₄ Cl ₃ SSiMe ₂ H	4.05 g. 83% recovered
2-(Me ₂ SiH)C ₄ Cl ₂ S- (Me ₂ SiH)-5 (0.02)	n-BuLi (0.02)	-70	2 hr. ^d	CO ₂	2-C ₄ Cl ₂ HSCOOH	3.0 g. 72%
2-(Me ₂ SiH)C ₄ Cl ₂ S- (Me ₂ SiH)-5 (0.02)	n-BuLi (0.04)	0	4.5 hr.	CO ₂	2-(COOH)C ₄ Cl ₂ S- (COOH)-5	4.2 g. 87%
2-(Me ₂ SiH)C ₄ Cl ₂ S- (Me ₂ SiH)-5 (0.02)	EtMgBr (0.04)	30	80 hr.	---	2-(Me ₂ SiH)C ₄ Cl ₂ S- (Me ₂ SiH)-5 ^e	
C ₆ F ₅ SiMe ₂ H (0.02)	n-BuLi (0.02)	-70	1 hr.	CO ₂	C ₆ F ₅ COOH	3.3 g. 80%
4-C ₅ Cl ₄ NSiMe ₂ H (0.02)	n-BuLi (0.02)	-70	40 min.	CO ₂	4-C ₅ Cl ₄ NCOOH	5.2 g. 86% ^f
C ₆ Cl ₅ SiMe ₂ H (0.02)	n-BuLi (0.02)	-15	3.5 hr.	CO ₂	Mixtures of Tars and Some Acid Products.	
C ₆ Cl ₅ SiMe ₂ H (0.02)	n-BuLi (0.04)	25	2 hr.	Me ₂ HSiCl	Mixture of Tars. IR shows only weak Si-H stretch.	

Table XIII continued

Silane (Mole)	RM (Mole)	Temp. (°C) (Maximum)	Time	Derivatizing Reagent	Products ^a	Yield ^b
$C_6Cl_5SiMe_2H$ (0.02)	$n-BuLi$ (0.02)	0	---	Me_3SiCl	Mixture of $C_6Cl_5SiMe_3$ 62% $p-Me_3SiC_6Cl_4-SiMe_2H-p$ 27% 5.8 g.	
$C_6Cl_5SiMe_2H$ (0.02)	$MeLi$ (0.02)	-70	2 hr.	Me_3SiCl	$C_6Cl_5SiMe_3$	4.9 g. 76%
$C_6H_5SiMe_2H$ (0.04)	$n-BuLi$ (0.04)	10	16 hr.	---	$C_6H_5SiMe_2Bu$	6.6 g. 86% ^h
$C_6H_5SiMe_2Bu$ (0.02)	$n-BuLi$ (0.02)	30	24 hr.	---	No reaction	
$2-C_4Cl_3SSiMe_3$ (0.025)	$n-BuLi$ (0.025)	-70	1 min.	CO_2	$2-(SiMe_3)C_4Cl_2S-$ $(COOH)-5$	6.0 g. 91% ⁱ
$2-C_4Cl_3SSiMe_3$ (0.02)	$n-BuLi$ (0.04)	25	87 hr.	CO_2	$2-(SiMe_3)C_4Cl_2S-$ $(COOH)-5$	2.6 g. 48%
$2-C_4Cl_3SSiMe_3$ (0.02)	$n-BuMgBr$ (0.02)	60 ^c	20 hr.	---	$2-C_4Cl_3SSiMe_3$	4.7 g. 91% recovered

^a Products were identified by comparison with authentic samples (mixed M.P. and IR spectra).

^b Based on Mole of starting silane.

^c Solvent was THF.

^d Reaction was complete in 20 min. (VPC). The second $SiMe_2H$ was cleaved by hydrolysis during work-up.

^e Product had other materials present. These were of longer retention time in the VPC and may have been the ethylated silanes.

Table XIII continued

f No evidence of other isomers.

g Percentages determined by VPC analysis on a 4 ft., Silicone Gum Rubber (15%) on Chromosorb W.

h $n_D^{20} = 1.4920$ cited $n_D^{20} 1.4920$. Identical retention time with material prepared on a small scale from PhMe_2SiCl and $n\text{-BuLi}$.

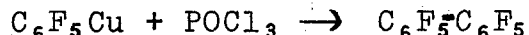
i Analysis Found: Cl 26.40%, Calc. for $\text{C}_8\text{Cl}_2\text{H}_{10}\text{O}_2\text{SiS}$: Cl 26.34%.

SECTION IX

COUPLING REACTION OF SOME POLYHALOARYLMETALLIC COMPOUNDS WITH PHOSPHORYL CHLORIDE

1. INTRODUCTION AND DISCUSSION

This particular reaction was encountered accidentally and incidental to an otherwise standard procedure. In connection with the preparation of some perhalogenated ketones we needed the perhalogenated acid chloride for a standard reaction with an organocopper compound. On working up the reaction mixture of a carboxylic acid with PCl_5 we observed a small quantity of a R_3PO product. In trying to explain this we reasoned that in some way POCl_3 appeared to have formed, and this probably was the intermediate inorganic compound which had undergone reaction with the organocopper compound. We soon found that this was not the case with our perhaloarylcopper compounds which, on reaction with POCl_3 , gave no significant or demonstrable quantity of the R_3PO type. Instead the chief product was formed from some sort of a coupling reaction to give a bi-aryl type:



in 53% and 48.5% yields. With the pentachlorophenylcopper, the yield of perchlorobiphenyl was 36%; and the yields of (4- $\text{C}_5\text{Cl}_4\text{N}$)-(4- $\text{C}_5\text{Cl}_4\text{N}$) from (4- $\text{C}_5\text{Cl}_4\text{N}$)Cu were 21% and 18%. Under essentially similar conditions, (2- $\text{C}_4\text{Cl}_3\text{S}$)Cu afforded 2,2'-hexachlorobithienyl in only 5-7% yield. However, the yield increased to 43% in THF-ether mixture. It is interesting to note that the products from the phenylcopper complex were: the expected Ph_3PO (11% and 13%), and Ph-Ph (35% and 37%). It seemed appropriate to carry out a reaction with the di-copper derivative of 3,4-dichlorothiophene, (3,4- $\text{C}_4\text{Cl}_2\text{S}$)(Cu) $_2$. Here also no phosphorus oxide type compound appeared to have formed, but the yield of what undoubtedly is the polymeric bi-aryl type (with chlorine atoms in the 3- and 4-positions of the thiophene nucleus) was only 10%. However, in order to get a corresponding product for purposes of comparison, a conventional coupling reaction was made between 3,4-dichloro-2,5-dilithiothiophene with cupric chloride, and the yield of the same (or same type) of polymeric material was quite satisfactory.

2. EXPERIMENTAL

All reactions were performed under a static pressure of dry oxygen-free nitrogen. Tetrahydrofuran was dried over sodium wire and further distilled from sodium-benzophenone ketyl. Magnesium turnings from the Mallinckrodt Chemical Works were heated in an oven at 120°C, prior to use. *n*-Butyllithium in hexane was from Foote Mineral Co. Copper(I) chloride was purified as reported²¹. Pentachlorobenzene (Olin Chemicals, Olin Mathiesen Chemical Corporation), pentafluorobenzene (Whittaker), pentachloropyridine (Olin Chemicals, Olin Mathiesen Chemical Corporation), and tetrachlorothiophene (Hooker Ind. Chem. Div.) were used for the preparation of perhaloaryl copper compounds, without further purification.

IR spectra were determined as thin films of nujol mull on sodium chloride plates, using a Perkin-Elmer Model 21 Spectrophotometer. VPC analyses were carried out on an F and M Model 500 Gas Chromatograph using a 4' column packed with 15% Silicon Gum Rubber on Chromosorb W, 60-80 mesh.

a. Preparation of copper compounds

The following compounds were prepared by reported procedures: phenylcopper (see this report, Section X); pentafluorophenylcopper²³; pentachlorophenylcopper²³; tetrachloro-4-pyridylcopper⁴; trichloro-2-thienylcopper (see this report, Section VI); and 2,5-bis(copper(I))-3,4-dichlorothiophene (see this report, Section VII).

b. Reaction of perhaloaryl copper compounds with POCl₃

To the perhaloaryl copper compound (0.05 mole) was added POCl₃ (2.56 g., 0.017 mole) in THF, dropwise, at 0°C. The reaction mixture was stirred for ~ 48 hr. at room temperature, the solvent removed under reduced pressure, and the residue extracted with a hot benzene-ether mixture. The benzene-ether extract was washed with aqueous ammonium hydroxide to remove copper salts, dried over anhydrous sodium sulfate, and the solvents were removed under reduced pressure. The crude product was chromatographed over silica gel. Each compound was identified by m.p. and mixture m.p., superimposable IR's, and identical retention volumes on a VPC instrument, using an authentic sample. The results are summarized in Table XIV.

Table XIV. Reaction of Various Copper Compounds With POCl_3

Copper Compound ^a	Product(s)	Yield (%)	m.p. (°C)	Remarks
$\text{C}_6\text{H}_5\text{Cu}$	i $\text{C}_6\text{H}_5\text{-C}_6\text{H}_5$ ii $(\text{C}_6\text{H}_5)_3\text{PO}$	35-37 11-13	69-70 155-156	--- ---
$\text{-C}_6\text{F}_5\text{Cu}$	$\text{C}_6\text{F}_5\text{-C}_6\text{F}_5$	53, 48.5	68-69	---
$\text{C}_6\text{Cl}_5\text{Cu}$	$\text{C}_6\text{Cl}_5\text{-C}_6\text{Cl}_5$	36	308-310	---
$(4\text{-C}_5\text{Cl}_4\text{N})\text{Cu}$	$4\text{-C}_5\text{Cl}_4\text{N-C}_5\text{Cl}_4\text{N-4}$	21 ^b , 18 ^c	226-228	---
$(2\text{-C}_4\text{Cl}_3\text{S})\text{Cu}$	$2\text{-C}_4\text{Cl}_3\text{S-C}_4\text{Cl}_3\text{S-2}$	5-7, 43 ^d (39, 43 ^d)	189-190	---
$(2\text{-C}_4\text{Cl}_3\text{S})\text{Cu}^{\text{e}}$	i $2\text{-C}_4\text{Cl}_3\text{S-C}_4\text{Cl}_3\text{S-2}$ ii $(2\text{-C}_4\text{Cl}_3\text{S})\text{H}$	15 27	189-190 ---	Identified by VPC, yield by VPC using Absolute Method
$(2,5\text{-C}_4\text{Cl}_2\text{S})\text{Cu}_2$	f	---	---	A product (10%) was isolated, the nature of which is yet unknown. It may be the coupled polymer having the following units: [$\text{-3,4-C}_4\text{Cl}_2\text{S-}$] _n .

Footnotes:

^a All the copper compounds were prepared from the corresponding lithium compounds and cuprous chloride in THF, unless otherwise mentioned.

Table XIV Continued

- b The crude product (~ 52%) contained tetrachloro-4H-pyridine and octachloro-4,4'-bipyridyl. The yield has been calculated from VPC chromatograms.
- c Yield when (4-C₅Cl₄N)MgCl was used for the preparation of (4-C₅Cl₄N)Cu.
- d The copper compound was prepared in THF-ether (2:1) mixture. The yield increased to 43% when the reaction mixture was refluxed for nearly 10 hr. following 12 hr. of stirring after complete addition of POCl₃.
- e Insufficient POCl₃ (approx. 1/3 of the stoichiometric amount) was used.
- f The major peaks in the finger-print region of its IR were found to be identical with the product obtained by M. R. Smith, Jr. from the reaction of 3,4-dichloro-2,5-dithiophene with cupric chloride. This might be expected to be a polymer containing 3,4-dichloro-2,5-thienylene units such as: $[-3,4-C_4Cl_2S-]_n$.

SECTION X

PREPARATION OF PERHALOARYL IODIDES VIA PERHALOORGANOMETALLIC COMPOUNDS AND IODINE

1. INTRODUCTION AND DISCUSSION

Incidental to our studies concerning the synthesis of various thermally stable compounds we have prepared a number of organic iodides by iodinating the corresponding copper compounds, and it has been observed that this reaction may be used to prepare several aryl iodides, particularly perhaloaryl iodides, in synthetically useful yields.

Attempts to prepare pentachloriodobenzene, tetrachloro-4-iodopyridine and trichloro-2-iodothiophene by reacting an appropriate perchloro compound with anhydrous sodium iodide in refluxing acetone or in refluxing dimethylformamide were not rewarding. The iodination of pentachlorophenylmagnesium chloride, tetrachloro-4-pyridylmagnesium chloride, and trichloro-2-thienylmagnesium halide gave good yields (66-70%) of the corresponding iodides. This method, however, is complicated by the inconvenience of the reverse addition, and also the yields of various iodides by this method were always 10-20% lower than those obtained by the iodination of the corresponding copper compounds.

The iodination of the aryl- and perhaloaryl- copper compounds, which may be a preferred method for the preparation of the corresponding iodides, involves the addition of solid iodine in bulk and at one time to an arylcopper compound (or complex) prepared by reacting the corresponding aryllithium or -magnesium halide with copper(I) chloride in THF or copper(I) iodide or bromide in ether or THF. It is observed that the copper(I) chloride-THF combination for the preparation of the copper compounds always gives the highest yield of the iodides. Nothing is to be gained by using excess iodine. In fact, the yield of pentachlorophenyl iodide drops by a few percent when 30% excess iodine is used. The iodination reactions are carried out at 0°C or at ambient temperatures depending upon the thermal stability of the copper compounds. Lower temperatures (-15° or -78°C) or slow additions of iodine in solution with THF or benzene instead of bulk addition at one time do not improve the yield.

This method of preparation of the organic iodides from the copper compounds is applicable not only to phenyl- and perhalophenyl- copper compounds and their pyridyl and thienyl counterparts but also to a dicopper compound such as dichloro-2,5-dicopperthiophene to give dichloro-2,5-diiodothiophene in good yield.

Alkylcopper compounds such as methylcopper or *n*-butylcopper are found to give the corresponding alkyl iodides in 64-75% yields, although there are better methods of preparing them in higher yields.

The high yield of iodobenzene may indicate that the reaction by which the copper compound is formed and its subsequent reaction with iodine are almost quantitative. Iodination reactions may thus provide a method of estimating some copper compounds without actually isolating them. The relatively lower yields of other aryl iodides may be due to the experimental difficulties in effecting a complete conversion of the perhaloarenes to the corresponding aryllithium or arylmagnesium halides; and, indeed, some unreacted polyhaloarenes are always recovered. Moreover, the thermal stability of these precursors of the copper compound may, in part, be responsible for the poorer yields.

2. EXPERIMENTAL

The reactions described here were conducted in an oxygen-free, dry nitrogen atmosphere. The solvents were dried over sodium wire and further purified by distilling them from sodium-benzophenone ketyl. *n*-Butyllithium in hexane, methyllithium in ether, and phenyllithium in ether-benzene were from the Foote Mineral Co. These lithium reagents were used at the strength determined by the supplier. Anhydrous copper(I) chloride (A.R. grade) was from Mallinckrodt Chemical Works and was purified²¹ prior to use. Anhydrous copper(I) bromide was prepared and purified by a reported procedure. Copper(I) iodide was from Alfa Inorganic Chemicals and was used without further purification. VPC analyses were carried out on an F and M model 500 Gas Chromatograph, using 4', 15% Silicon Gum Rubber on Chromosorb W (60-80 mesh).

The yields were computed on the amount of starting polyhaloarenes; in the case of a product containing phenyl, methyl or *n*-butyl groups the computations were based on the amount of the respective starting lithium reagents.

a. Preparation of polyhaloarylmetallic compounds

The following were prepared by the published procedures: pentachlorophenylmagnesium chloride³⁴ and the corresponding lithium⁴² and copper²³ compounds, tetrachloro-4-pyridylmagnesium chloride² and the corresponding copper compound⁴, and pentafluorophenylmagnesium chloride^{24a} and the corresponding lithium⁴³ and copper²³ compounds. Trichloro-2-thienylmagnesium halide was prepared in THF from tetrachlorothiophene (*x* moles), magnesium (2*x* g. atoms) and ethylene bromide (*x* moles); and the corresponding copper

compound was made in the usual way by reacting the Grignard reagent with copper(I) chloride at room temperature. The lithium and Grignard reagents were made on a 0.05 molar scale and were used directly for the synthesis of the corresponding copper compounds without determining the concentration.

b. Preparation of alkylcopper compounds

Methylcopper⁴⁴ and *n*-butylcopper⁴⁵ were prepared by following the published procedures which consisted of the slow addition of a selected organolithium reagent (x moles) to copper(I) iodide (x moles) in ether at -15°C and stirring the mixture until Color Test I was negative. The copper compound was used immediately after the preparation.

c. Preparation of phenylcopper

The method of preparation was essentially the same as that for the alkylcopper compounds except that phenyllithium was used in place of an alkylolithium compound. Phenylcopper prepared from copper(I) chloride - THF combination gave a clear brown solution in THF. Table XVII shows the yields of iodobenzene, under different experimental conditions.

d. Preparation of 'ate' complexes

Lithium dimethylcuprate⁴⁴, lithium di-*n*-butylcuprate⁴⁵ and lithium diphenylcuprate⁴⁶ were prepared by the reported procedures which consisted of the dropwise addition of an appropriate organolithium reagent (2x moles) to copper(I) iodide (x moles) at -15°C. Chloromagnesium *bis*(pentafluorophenyl)cuprate was prepared in a similar manner using pentafluorophenylmagnesium chloride in place of the corresponding lithium reagent. It did not respond to Color Test I. Lithium *bis*(pentafluorophenyl)cuprate and its penta-chlorophenyl analog were prepared in the same way except that the reaction temperature was -78°C instead of -15°C. Lithium *bis*-(pentachlorophenyl)cuprate gave Color Test I, whereas lithium *bis*(pentafluorophenyl)cuprate did not.

e. Iodination of copper compounds

(1) Iodination of aryl- and polyhaloaryl- copper compounds

Solid iodine (x moles) was added at one time to a polyhaloaryl-copper compound prepared from a polyhaloarene (x moles). The reaction mixture was stirred at the ambient temperature for 2 hr., hydrolyzed with ammonium chloride - aqueous ammonia solution, extracted with ether or benzene and the ether or benzene extract was dried over anhydrous sodium sulfate. The solid obtained after removal of the solvent was further purified by chromatography on a

silica gel column and/or by subsequent recrystallization from carbon tetrachloride. Following this procedure, pentachloroiodobenzene, m.p. 210°C (cited⁴⁷: 207.5-208°C) (identified by mixed m.p., superimposable IR and also by VPC of an authentic sample); tetrachloro-4-iodopyridine, m.p. 201-202°C (identified by underpressed mixed m.p., IR and VPC of an authentic sample prepared⁴⁸ by the iodination of the corresponding Grignard reagent); and trichloro-2-iodothiophene, m.p. 49-50°C (cited²⁶: 50-51°C) were prepared.

Phenylcopper and pentafluorophenylcopper were iodinated at 0°C, but the yield of iodobenzene was higher by 7% when phenylcopper was iodinated at -78°C. Both iodobenzene and pentafluoroiodobenzene were purified by fractional distillation under reduced pressure: iodobenzene, b.p. 84-86°C/35 mm., n_D^{20} 1.6163 (cited⁴⁹: b.p. 187.7°C, n_D^{18-20} 1.6189); pentafluoroiodobenzene, b.p. 76-78°C/35 mm., n_D^{20} 1.4955 (cited⁵⁰: bp. 77-78°C/35 mm., n_D^{20} 1.4965). See Tables for the yields of the iodides under various experimental conditions.

(2) Iodination of alkylcopper compounds

Methyl- and n-butyl- copper compounds were iodinated exactly as mentioned above except that the iodination temperature was -78°C instead of room temperature. The products were estimated by VPC (4', 5% Crosslinked Diethylene Glycol Adipate, LAC - 446, on Fluoropak, 80 mesh) using n-heptane as an internal standard.

(3) Iodination of 'ate' complexes

All 'ate' complexes were iodinated at -78°C by the addition of solid iodine (two equivalents) in bulk and at one time. The reaction mixture was stirred at -78°C and allowed to come to room temperature slowly. The work-up procedures were similar to those for the respective uncomplexed copper compounds (see (2)).

f. Iodination of perhaloarylmagnesium halides

All reactions were carried out on a 0.05 molar scale. Two types of addition were tried: the Grignard reagent to iodine in benzene or to solid iodine, and the reverse. Pentachlorophenylmagnesium chloride and trichloro-2-thienylmagnesium halide were iodinated at 0°C, whereas tetrachloro-4-pyridylmagnesium chloride was iodinated at -10°C. The work-up procedures for these reactions were similar to those for the iodination of the corresponding copper compounds. The identity of the various iodides was established by mixed m.p. with authentic samples. The yields of the iodides are shown in Table XV.

g. Reactions of perhaloarenes with anhydrous sodium iodide

A mixture of perchloroarene (x moles) and anhydrous sodium iodide (4x moles) in dry acetone (275 ml.) or in dry dimethylformamide (DMF) (250 ml.) was refluxed up to 75 hr., cooled to room temperature, and digested with water. The organic material was then extracted with C_6H_6 or pet. ether. Table XXI gives the details of the experimental conditions together with the yields of various products.

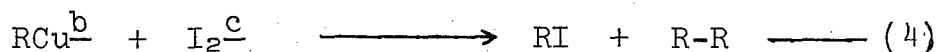
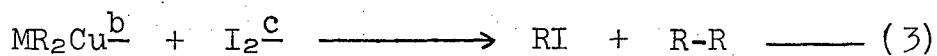
Table XV. The yields (%) of different iodides by the reaction:



R =	M = $\frac{\text{MgX}^{\text{a}}}{\text{RI}}$	M = Cu	
		RI	Other products
C_6H_5	90 ¹¹	94 ^b	R-R^{bc} , 3
C_6F_5	46.7 ³⁹	84 ^d	R-R^{d} , 8
C_6Cl_5	70 (63) ^e	82 ^f	R-R , 4 ; RCl , 3
$\text{C}_5\text{Cl}_4\text{N}$	67 ^g (65) ⁴⁰	77 ^f	RCl , 4
$\text{C}_4\text{Cl}_3\text{S}$	66-70 (63)	85 ^f	R-R^{c} , 2; RCl^{b} , 2
$\text{C}_4\text{Cl}_2\text{S}$	—	62	—
CH_3	—	65-70 ^h	—
$\text{n-C}_4\text{H}_9$	—	64 ^h	R-R , 24 ^h

^a The Grignard reagent was always added dropwise to the iodine solution in dry benzene unless otherwise mentioned. ^b Based on the amount of starting phenyllithium. ^c Estimated by VPC using durene as the internal standard. ^d Based on the amount of starting polyhaloarene. ^e When a benzene solution of iodine was added to the Grignard reagents the yields of RI are in parentheses. ^f Based on the amount of polyhaloarene consumed. ^g When tetrachloro-4-pyridylmagnesium chloride was added dropwise to solid iodine rather than to a benzene solution of iodine, the yield of the corresponding iodide was 54%. When solid iodine was added in bulk and at one time to the same Grignard reagent the yield of the iodide was 48%. ^h Estimated by VPC using *n*-heptane as the internal standard. The yields are based on the amount of the respective starting lithium reagent.

Table XVI. The yields (%) of RI and R₂^a via (3) compared with the yields via (4)



R =	Reaction (3)		Reaction (4)
	M = Li	M = MgCl	
CH ₃	50-60 ^d (---)	—	65-75 ^d (---)
<u>n</u> -C ₄ H ₉	46 ^d (52)	—	64 ^d (24)
C ₆ H ₅	86 ^d (12)	—	90 ^d (9)
C ₆ F ₅	59 ^e (28)	47 ^e (37)	72-73 ^e (9-11)
C ₆ Cl ₅	61 ^e (22)	—	78 ^e (10)

^a The yields of R-R are in parentheses.

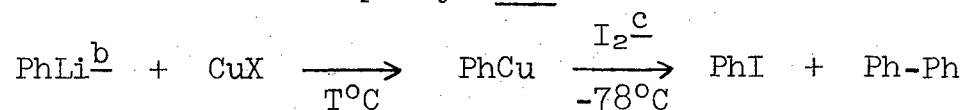
^b The copper compounds or the 'ate' complexes were prepared using copper(I) iodide.

^c A stoichiometric amount of solid iodine was added in bulk and at one time, the reaction temperature being -78°C.

^d Based on the starting lithium reagent.

^e Based on the starting polyhaloarene.

Table XVII. Effects of temperatures, solvent and the type of copper(I) halide on the yields (%)^a of iodobenzene and biphenyl via



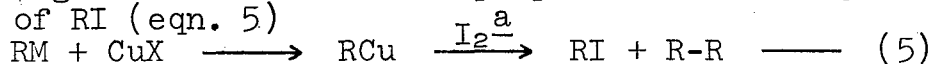
CuX	T = 0°C		T = -15°C	
	PhI	Ph-Ph	PhI	Ph-Ph
CuCl in ether	Trace - 14	70-80	39-43	51-56
CuCl in THF	-----	-----	94	4
CuBr in ether	91	2	-----	-----
CuI in ether	83	10	87-90	7-9
CuI in THF	-----	-----	91	2

^a Based on the amount of starting phenyllithium.

^b Phenyllithium in ether-benzene was obtained commercially and used at the strength determined by the supplier.

^c Solid iodine was added in bulk and at one time. When added in solution with THF- benzene or benzene under the same conditions no noticeable variations in the yield of PhI or Ph-Ph were observed.

Table XVIII. Effects of various copper(I) halides and various organometallics used to prepare RCu on the yields of RI (eqn. 5)



RM	CuX	RI (%)	R ₂ (%)
C ₆ H ₅ Li	CuCl	94 ^b	3
C ₆ H ₅ Li	CuI	91 ^b	2
C ₆ F ₅ MgCl	CuCl	84 ^c	8
C ₆ F ₅ MgCl	CuI	72-73 ^c	9-11
C ₆ Cl ₅ Li	CuCl	82 ^d	4
C ₆ Cl ₅ Li	CuI	78 ^d	10
C ₆ Cl ₅ MgCl	CuCl	77 ^e	5

^a Solid iodine in stoichiometric amount was added in bulk and at one time.

^b Phenylcopper was prepared in THF at -15°C but iodinated at -78°C.

^c Pentafluorophenylcopper was prepared and iodinated in THF at 0°C.

^d Pentachlorophenylcopper was prepared at -78°C but iodinated at room temperature.

^e Pentachlorophenylcopper was prepared and iodinated at room temperature.

Table XIX. Effects of solvent for iodine and also the amount of iodine on the yields of RI via

$$\text{RCu} \xrightarrow{\text{I}_2} \text{RI} + \text{R-R}^{\text{a}}$$

RCu	(%) RI		
	Stoichiometric amount of solid iodine	30% excess iodine (solid)	Iodine in THF-PhH (Stoichiometric amount)
$\text{C}_6\text{H}_5\text{Cu}^{\text{b}}$	91 (2)	----	87 (7)
$\text{C}_6\text{F}_5\text{Cu}^{\text{c}}$	72-73 (9-11)	----	75 (10)
$\text{C}_6\text{Cl}_5\text{Cu}^{\text{d}}$	82 (4)	76 (--)	----

^a The yields of R-R are in parentheses.

^b Phenylcopper was prepared in THF at -15° (from PhLi and CuI) but iodinated at -78°C.

^c Pentafluorophenylcopper was prepared from pentafluorophenylmagnesium chloride and CuI in THF at 0°C and iodinated at the same temperature.

^d Pentachlorophenylcopper was prepared from pentachlorophenyllithium and CuCl at -78°C but iodinated at room temperature.

Table XX. Variation in the yields of RI with the change of temperature of iodination^a

RCu	% RI	
	0°C	-78°C
C ₆ H ₅ Cu ^b	87 ^c (4) ^d	94 (3)
C ₆ F ₅ Cu ^e	72-73 (9-11)	70 ^f (9)

^a Solid iodine in stoichiometric amount was added in bulk and at one time for iodination.

^b Phenylcopper was prepared from phenyllithium and CuCl in THF at -15°C.

^c This 7% lower yield of iodobenzene at 0°C as compared with the yield at -78°C was probably due to the thermal instability of phenylcopper at 0°C. See Table XVII.

^d The yields of R-R are in parentheses.

^e Pentafluorophenylcopper was prepared from pentafluorophenylmagnesium chloride and CuI in THF at 0°C.

^f The yield of pentafluoriodobenzene was 72% when pentafluorophenylcopper was prepared from pentafluorophenylmagnesium chloride and CuI in THF at -15°C.

Table XXI. Reaction of perchloroarenes with anhydrous sodium iodide

Perchloro- arene	Mole of per- chloro- arene	Medium	Reflu- xing period (hr.)	Solvent for extract- ion	Pro- ducts (yield (%) ^a)	m.p. °C	Reported m.p. °C
C ₆ Cl ₆	0.05 ^d	Acetone	12	Benzene	C ₆ Cl ₆ 95	226- 227	227
C ₆ Cl ₆	0.05 ^d	DMF	48	Benzene	C ₆ Cl ₆ 90	226- 227	226- 227
C ₄ Cl ₄ S	0.05 ^d	Acetone	75	Pet. Ether (b.p. 60-70°C)	C ₄ Cl ₄ S ^b 98	—	—
C ₄ Cl ₄ S	0.05 ^d	DMF	24	Pet. Ether (b.p. 60-70°C)	C ₄ Cl ₄ S ^b 98	—	—
C ₅ Cl ₅ N	0.1 ^e	Acetone	48	Benzene	C ₅ Cl ₅ N 96	125- 126	125- 126
C ₅ Cl ₅ N	0.1 ^e	DMF	48	Benzene	4-(C ₅ Cl ₄ N)I 16 ^c	202	202

^a Based on the starting amount of perchloroarene.

^b Estimated by VPC with durene as an internal standard.

^c Identified by mixed m.p. with a sample prepared by the iodination tetrachloro-4-pyridylmagnesium chloride⁴⁸.

^d 0.25 mole NaI was used.

^e 0.40 mole NaI was used.

SECTION XI

UNSYMMETRICAL PERHALO ANALOGS OF BIPHENYL

1. INTRODUCTION AND DISCUSSION

We have been interested in the synthesis of useful, thermally stable compounds having polyfunctional groups. One way of approaching our objective was by the synthesis of perhalogenated biaryls especially those containing unsymmetrical nuclei such as $C_6Cl_5C_6F_5$ or C_6X_5R (where $X = Cl$ or F and R is either a perchloropyridyl or perchlorothieryl group). This choice was based on several reasons: (1) perhaloaryl nuclei contribute to thermal stability; (2) perhalo heterocyclic nuclei are generally more stable than perhalo homocyclic nuclei; (3) the perhaloaryl nuclei provide a promising route to the introduction of functional groups such as HMe_2Si which provide access to useful polymers; and (4) unsymmetrical perhalobiphenyl analogs might not only be expected to take on the superior thermal stability of biphenyl types, but should additionally have useful lower melting point than the symmetrical analogs of perhalobiaryls.

2. EXPERIMENTAL

The reactions described here were conducted under a positive pressure of oxygen-free, dry nitrogen. The solvents were purified by drying over sodium wire and finally by distilling them from sodium-benzophenone ketyl. All temperatures reported are uncorrected. The yields of the products are based on the starting polyhaloarene.

a. Preparation of polyhaloarylcopper compounds

Pentafluorophenylcopper²³, pentachlorophenylcopper²³, tetrachloro-4-pyridylcopper²³ and trichloro-2-thienylcopper (Section VI) compounds were prepared by the reported procedures.

b. Preparation of perhaloaryl iodides

Pentafluorophenyl iodide, pentachlorophenyl iodide, tetrachloro-4-iodopyridine and trichloro-2-iodothiophene were prepared by iodinating (see SECTION X) the corresponding copper compounds.

c. Preparation of unsymmetrical perhalobiaryls

To a perhaloarylcopper compound (prepared in THF from 0.025 moles of perhaloaryl-lithium or -magnesium halides and 0.025 mole of copper(I) chloride or copper(I) iodide) was added 0.025 mole of perhaloaryl iodide (containing a different perhaloaryl group from

that of the perhaloaryl copper) in dioxan or 2,2,4,4-tetramethyl-tetrahydrofuran (TM-THF). The low boiling liquids were distilled off and the mixture was heated at 100°C (dioxan) or 110°C (TM-THF) for a period of 40 hr. or slightly less. The reactions were monitored by VPC. At the end of this period, the reaction mixture was hydrolyzed with $\text{NH}_4\text{Cl}/\text{aq. NH}_3$ solution and the organic material was collected in benzene. The benzene extract was washed with $\text{NH}_4\text{Cl}/\text{aq. NH}_3$ three times or until all copper halides were removed, and then washed with water, dried over anhydrous sodium sulfate, and the solvent distilled. The white solid obtained was generally a mixture of products which was separated by column chromatography (Silica Gel) and successive recrystallization from suitable solvents. Table XXII shows the experimental conditions for the preparation of various unsymmetrical perhalobiaryls together with their yields, and Table XXIII compares the m.p. of the unsymmetrical perhalobiaryls with those of symmetrical perhalobiaryls and Table XXIV shows some spectral data.

Table XXII. Some unsymmetrical perhalobiaryls via perhaloaryl copper compounds and perhaloaryl iodides

Copper Compounds ^a	Iodides	Temp. (°C)	Time (hr.)	Unsymmetrical biaryl (yield%) ^b	Crystallizing Solvent	Other Products (yield %) ^c
(2-C ₄ Cl ₃ S)Cu	C ₆ F ₅ I ^c	100	40	(2-C ₄ Cl ₃ S)-C ₆ F ₅ (50)	Pet. ether (60-80°C)	(2-C ₄ Cl ₃ S) ₂ , 2.0 3; (C ₆ F ₅) ₂ , 1.25 g; traces (VPC) of 2-C ₄ Cl ₃ SI and C ₆ F ₅ I.
C ₆ Cl ₅ Cu	C ₆ F ₅ I ^c	100	40	C ₆ Cl ₅ -C ₆ F ₅ (46)	Pet. ether (60-80°C)	(C ₆ Cl ₅) ₂ , 22; (C ₆ F ₅) ₂ , 6, C ₆ F ₅ I, 7; and a trace (VPC) of C ₆ Cl ₅ I.
(4-C ₅ Cl ₄ N)Cu	C ₆ F ₅ I	100	40	(4-C ₅ Cl ₄ N)-C ₆ F ₅ (28)	Pet. ether (60-80°C)	(4-C ₅ Cl ₄ N) ₂ , 3; (C ₆ F ₅) ₂ , 1; 4-C ₅ Cl ₄ NI, 1; C ₆ F ₅ I, 1 and C ₅ Cl ₅ N, 1 (VPC).
C ₆ Cl ₅ Cu	(4-C ₅ Cl ₄ N)I	100	40	(4-C ₅ Cl ₄ N)-C ₆ Cl ₅ (48)	Benzene	----
(2-C ₄ Cl ₃ S)Cu	(4-C ₅ Cl ₄ N)I ^d	110	40	(2-C ₄ Cl ₃ S)-(4-C ₅ Cl ₄ N) (40)	Benzene	(2-C ₄ Cl ₃ S) ₂ , 10; (4-C ₅ Cl ₄ N) ₂ , trace (VPC); 4-C ₅ Cl ₄ NI, 2; a trace of 2-C ₄ Cl ₃ SI.
(2-C ₄ Cl ₃ S)Cu	C ₆ Cl ₅ I	100	40	C ₆ Cl ₅ -(2-C ₄ Cl ₃ S) (56)	Pet. ether (60-80°C) -Benzene	(2-C ₄ Cl ₃ S) ₂ , 5; (C ₆ Cl ₅) ₂ , 10; C ₆ Cl ₅ I, 5; No 2-C ₄ Cl ₃ SI.
C ₆ Cl ₅ Cu	(2-C ₄ Cl ₃ S)I ^c	100	40	C ₆ Cl ₅ -(2-C ₄ Cl ₃ S) (32)	Pet. ether (60-80°C) -Benzene	(2-C ₄ Cl ₃ S) ₂ , 22; (C ₆ Cl ₅) ₂ , 15.

^a 0.025 mole scale dioxan as solvent. ^b Based on the iodide. ^c Refluxed 24 hr. in THF; dioxan added as THF distilled. ^d TM-THF as solvent.

Table XXIII. Comparisons of the m.p. of Some Perhalogenated Symmetrical and Unsymmetrical Biaryls

Biaryl	M.P. (°C)
$[C_6H_5-C_6H_5]$	70.5
$C_6F_5-C_6F_5$	68-69
$C_6Cl_5-C_6Cl_5$	310
$(4-C_5Cl_4N)-(4-C_5Cl_4N)$	226-228
$(2-C_4Cl_3S)-(2-C_4Cl_3S)$	189.5-190
$C_6F_5-C_6Cl_5$	127
$C_6F_5-(4-C_5Cl_4N)$	105-106
$C_6F_5-(2-C_4Cl_3S)$	78.5
$C_6Cl_5-(4-C_5Cl_4N)^a$	222.5-223
$C_6Cl_5-(2-C_4Cl_3S)^b$	193-194
$(4-C_5Cl_4N)-(2-C_4Cl_3S)$	199

^a Mixed m.p. with $(4-C_5Cl_4N)_2$ was 178-190°C.

^b Mixed m.p. with $(2-C_4Cl_3S)_2$ was 160-180°C.

It will be noted from the footnotes accompanying the above table, that mixed melting points show no dimorphism.

Table XXIV. Some spectral data of various perhalogenated unsymmetrical biaryls

Biaryls	IR (cm. ⁻¹) ^a	Mass Spec. ^b	Mol. wt. (calc.) (Cl = 35.45)
C ₆ F ₅ -C ₆ Cl ₅	1653, 1597, 1543, 1520 { C ₆ F ₅ - }; 1344, 1304 { C ₆ Cl ₅ - }; 1081, 995 { C-F }; 758, 699, 655 { C-Cl }	-----	416.39
C ₆ F ₅ -(4-C ₅ Cl ₄ N)	1653, 1595, 1527 { C ₆ F ₅ - }; 1504, 1493, 1453 (C ₅ Cl ₄ N-); 1073, 985 (C-F); 757, 727, 673, 678 (C-Cl)	-----	382.93
C ₆ F ₅ -(2-C ₄ Cl ₃ S) ^c	1653, 1597 (C ₆ F ₅ -); 1538, 1325, 1316 (C ₄ Cl ₃ S-); 1064, 1036, 1027, 978.5 (C-F); 776, 769, 725 (C-Cl)	A number of peaks grouped around m/e 354 (M ⁺) hav- ing the character- istic isotope pat- tern for three Cl atoms, around 319 (M-Cl), around 300 (M-FC1), at 282 and 284 (M-Cl ₃)	353.53
C ₆ Cl ₅ -(4-C ₅ Cl ₄ N)	1563, 1548, 1520, 1379, 1355, 1332 (C ₅ Cl ₄ N- and C ₆ Cl ₅ - nuclei); 769, 755 (C-Cl)	A number of peaks grouped around m/e 465 (M ⁺) hav- ing the character- istic isotope pat- tern for nine Cl atoms, around 428 (M-Cl), around 395 (M-Cl ₂), around 216 (C ₅ Cl ₄ N ⁺)	465.20

Table XXIV. (Cont.)

$C_6Cl_5-(2-C_4Cl_3S)$	1550, 1321, 1311 (C_4Cl_3S-); 1359, 1342 (C_6Cl_5-); 714, 692, 660 (C-Cl)	A number of peaks grouped around m/e 436 (M^+) hav- ing the character- istic isotope pat- tern for eight Cl atoms, around 364 (M-Cl ₂), around 329 (M-Cl ₃), around 294 (M-Cl ₄)	435.80
$(4-C_5Cl_4N)-(2-C_4Cl_3S)^d$	1550, 1508, 1460, 1399, 1361, 1342 (C_5Cl_4N- and C_4Cl_3S- nuclei); 751, 737, 712 (C-Cl)	A number of peaks grouped around m/e 403 (M^+) hav- ing the character- istic isotope pat- tern for seven Cl atoms, around 366 (M-Cl), around 331 (M-Cl ₂), around 296 (M-Cl ₃), around 216 ($C_5Cl_4N^+$)	402.34

^a I.R. spectra were taken either as nujol mulls or as KBr pellets using a Perkin-Elmer Model 21 Spectrophotometer.

^b Mass Spectra were taken with an Atlas CH4 Spectrometer.

^c [Found: Cl, 30.00%. Calc. for $C_{10}Cl_3F_5S$: Cl, 30.08%.]

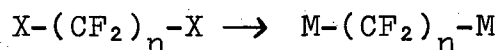
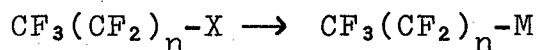
^d [Found: Cl, 61.37%. Calc. for C_9Cl_7NS : Cl, 61.68%.]

SECTION XII

CHLORINE-LITHIUM EXCHANGE UNDER VERY MILD CONDITIONS

1. INTRODUCTION AND DISCUSSION

Our extensive studies of several years ago showed that a halogen-lithium exchange reaction takes place with great difficulty and to a subordinate extent when the halogen is chlorine. Second, it is known that tetrachlorothiophene does react with *n*-butyllithium to give trichloro-2-thienyllithium. However, when one adds a tertiary amine such as triethylamine to such a system there is a pronounced increase in activity. In the case mentioned, the reaction goes: (a) neatly at -78°C ; (b) the reaction is complete in less than 10 min. at this temperature; and (c) the yield is in excess of 95% (based on the actual carboxylic acid in hand when the resulting trichloro-2-thienyllithium is carbonated). The reaction is being examined with some related types, and also with other tertiary amines such as tetramethylethylenediamine, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$, which is the conventional complexing agent with a reaction such as metalation. The uncommonly mild conditions and excellent yields of our chlorine-lithium or halogen-metal exchange do, of course, suggest their promise for exchanges of the following types:



2. EXPERIMENTAL

To a 500 ml. flask was added 0.05 mole (11.06 g.) of $\text{C}_4\text{Cl}_4\text{S}$, 200 ml. of ether and 0.05 mole (5.0 g.) of triethylamine. The mixture was cooled to -70°C and 0.05 mole of *n*-BuLi in hexane was added. An exothermic reaction set in at once. After 10 min. the reaction to produce trichloro-2-thienyllithium was essentially complete, as monitored by VPC (Silicone Gum Rubber). Carbonation after 20 minutes yielded 10.8 g. (95%) of trichloro-2-thiophene-carboxylic acid (melting and mixed m.p., $225\text{--}226^{\circ}\text{C}$).

In earlier experiments, it was observed that tetrachlorothiophene did not react with *n*-BuLi in ether/hexane to any appreciable extent at -70°C in the absence of Et_3N .

As expected, two equivalents of *n*-BuLi with Et_3N gave the 3,4-dichloro-2,5-dilithiothiophene but under essentially the same conditions and time as in the absence of Et_3N .

Table XXV: List of New Compounds

Compound	M.P. (°C) or B.P. (°C/mm. Hg)	Page
2,5-Dichloro-4-pyridinecarboxylic acid	222-3	6,10,12
2,5-Dichloro-4-pyridyltrimethylsilane	46-7 83/1.5 mm.	6,10,12
bis(2,5-Dichloro-4-pyridyl)dimethylsilane	107.5-8	6,10,12
2,5-Dichloro-4-pyridylphenylcarbinol	169-70	7,10,13
2,5-Dichloro-4-pyridyldiphenylcarbinol	128-9	7,10,13
2,5-Dichloro-4-acetylpyridine	86-7/0.75 mm.	7,11,14
2,5-Dichloro-4-benzoylpyridine	130-1	7,11,14
2,2'5,5'-Tetrachloro-4,4'-bipyridyl	121.5-2	7,11,14
3,5-Dichloro-4-pyridyltrimethylsilane	60-5/0.15 mm.	8
2,6-Difluoro-3-pyridyltrimethylsilane	74-6/16 mm.	8,9
Trichloro-2-thienyltrimethylsilane	73-4/0.5 mm.	22,26,30
Trichloro-2-thienylphenyldimethylsilane	127/0.15 mm.	22,27,30
Trichloro-2-thienyltriphenylsilane	110.5-111	22,27,30
Trichloro-2-thienyldimethylsilane	81-2/1.0 mm.	31
bis(Trichloro-2-thienyl)dimethylsilane	90-90.5	31
2,5-bis(Trimethylsilyl)dichlorothiophene	79/0.07 mm.	33
2,5-bis(Dimethylsilyl)dichlorothiophene	92/1.0 mm.	33
2-Allyltrichlorothiophene	64/0.5 mm.	42
2-Benzoyltrichlorothiophene	69-70	42
2-Phenyltrichlorothiophene	63.5-4	42

Table XXV (Contd)

Compound	M.P. (°C) or B.P. (°C/mm. Hg)	Page
<u>trans</u> -1,4-bis(Trichloro-2-thienyl)butene-1,4-dione	203-4	42
2,5-bis(Acetyl)dichlorothiophene	172.5-173.5	43
2-Trimethylsilyldichloro-5-thiophenecarboxylic acid	177.5-8	46, 48
2,3,4,5,6-pentachloro-2',3',4',5',6'-penta-fluorobiphenyl	127	66-70
4-Pentafluorophenyltetrachloropyridine	105-6	66-70
2-Pentafluorophenyltrichlorothiophene	78.5	66-70
4-Pentachlorophenyltetrachloropyridine	222.5-3	66-70
2-Pentachlorophenyltrichlorothiophene	193-4	66-69, 71
4-(Trichloro-2-thienyl)tetrachloropyridine	199	66-69, 71

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13. ABSTRACT			
<p>The primary objective is concerned with new or improved syntheses of organometallic and organometalloidal compounds containing polyfluoro and polychloro substituents. These versatile reagents are to be used for the preparation of thermally stable fluids, lubricants, etc. One of the goals is to make available organometallic compounds of general types such as $CF_3(CF_2)_n-M$ and $M-(CF_2)_n-M$, in which M represents a metal or a metalloid. In addition, perhaloorganometallic compounds containing heteronuclear systems such as pyridine and thiophene have been studied. These two studies admirably complement each other, for there has been developed from the perhalogenated thiophenes some novel and highly promising routes to the perhalogenated alkanes.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Organometallic Compounds Organometalloidal Compounds Organosilicon Compounds Perhaloarylmetallic Compounds Perhalogenated Heterocyclic Derivatives Halopyridines Perhalothiophene Derivatives Unsymmetrical Perhalogenated Biaryls Improvement of Halogen-Metal Exchange Conversion of $\text{-C-SiMe}_2\text{H}$ to -C-Li						

Unclassified

Security Classification